disperse phase (in $m^3/m^2 \cdot hour$); C_{di} and C_{df} are the initial and final concentrations of the dissolved substances in the disperse phase (in $kg\text{-}mole/m^3$).

The extraction coefficient was calculated from the following equation:

$$K_V = \frac{G}{V_{ef} \, \Delta C_m} \quad \frac{Kg\text{-}mole}{m^3 \cdot hr \cdot kg\text{-}mole/m^3} \qquad (2)$$

where G is the quantity of substance extracted (in kg-mole/hr) determined from the material balance equation (1); V_{ef} is the effective volume of the packing (in m^3); ΔC_m is the mean difference in concentrations produced in the process (in kg-mole/m^3).

The effective volume of the packing was determined from:

$$V_{ef} = F \cdot f \cdot H \; m^3 \qquad (3)$$

where F is the free volume of the packing (in m^3/m^3), f is the area of cross section of the column (in m^2), and H is the height of the column packing (in m).

In apparatus of the normal type, the effective volume of the packing was $V_{ef} = 0.00121\ m^3$, and when operating with columns having an increased separation volume, $V_{ef} = 0.00081\ m^3$.

The mean transference of the process ΔC_m was determined from the equation:

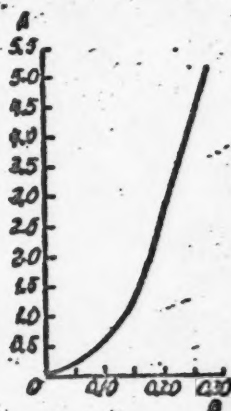$$\Delta C_m = \frac{\Delta C_I - \Delta C_F}{2.3 \log \frac{\Delta C_I}{\Delta C_F}} \qquad (4)$$

Fig.1. Equilibrium curves for the system water-acetic acid-benzene. A – C_V (in kg-mole/m^3); B – C_b (in kg-mole/m^3).

Fig.2. Equilibrium curves for the system HCl solution-phenol-benzene. A – C_b (in kg-mole/m^3); B – C_v (in kg-mole/m^3).
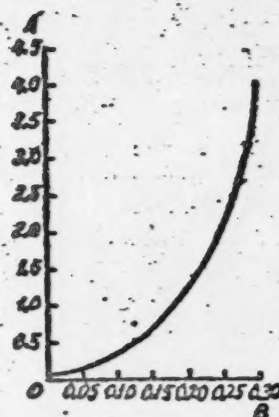

Fig.3. Equilibrium curves for the system HCl solution-phenol-chlorobenzene. A – C_x (in kg-mole/m^3); B – C_v (in kg-mole/m^3).

where C_I and C_F are the initial and final concentrations of the dissolved substance (in kg-mole/m^3): $\Delta C_m = C_I - C_{FR}$ and $\Delta C_F = C_F - C_{FR}$; C_{IR} and C_{FR} equilibrium concentration (in kg-mole/m^3).

The equilibrium curves for investigating the system are presented in Figs.1-3 [2]. The extraction coefficients were calculated for the phase in which the substance being extracted dissolved with more difficulty, and with which the interfacial tension was decisive.

For the system water-acetic acid-benzene the extraction coefficient was calculated for the benzene film.

For the system HCl solution-phenol-benzene and HCl solution-phenol-chlorobenzene, in view of the small value of the distribution coefficient, the partial extraction coefficients were first calculated, and then the total coefficient from the formula:

$$\frac{1}{K_O} = \frac{1}{mK_{11}} + \frac{1}{K_{12}} , \tag{5}$$

where K_O is the total extraction coefficient (in kg-mole/m^3·hour· kg-mole/m^3) K_{11} and K_{12} are the partial extraction coefficients for both films (in kg-mole/m^3· hour ·kg-mole/m^3); m is the mean slope of the equilibrium curves.

The mean slope of the equilibrium curves was determined for the systems investigated by graphical integration following the Gauss method. For the HCl solution-phenol-benzene system it was 13.44, and for the HCl solution-phenol-chlorobenzene system it was 10.63.

The efficiency of the packed columns can be expressed not only by the extraction coefficient but also by the integral of packing height determined from:

$$h_1 = \frac{H}{\int_{C_I}^{C_F} \frac{d_c}{C-Cp}} = \frac{V}{K_V} m , \tag{6}$$

where V is the volumetric flow rate of the phase for which the coefficient is calculated, related to the cross sectional area of the column (in m^3/m^2·hour); K_V is the extraction coefficient.

Analysis of the data obtained permits us to draw conclusions about the influence of different factors on the mass transfer in packed extraction columns.

Effect of separate factors on the mass transfer in extraction columns.

a) Effect of rate of flow and change of phase. The flow rate of the liquids is one of the basic factors conditioning mass transfer. The range over which the velocity was changed in our experiments was fairly wide (8-285 cm^3/min) permitting the investigation of the effect of small and large rates.

Usually the flow rate of the continuous phase was changed, keeping that of the disperse phase constant. This is exclusive of a series of experiments in which phenol was extracted with benzene from hydrochloric acid solutions, where the benzene was the continuous phase and was fed at constant rate while the rate of the hydrochloric acid solution, which was the disperse phase, was varied.

In Figs.4-7 are shown the effects of change of continuous phase rate on the extraction coefficient, from which it follows that the extraction coefficient increases markedly as the continuous phase rate increases. In Fig.4 the results of working up the experimental data for the system water-acetic acid-benzene as the dependence of the partial extraction coefficient, determined for the benzene film, on the change in the flow rate of the continuous phase are shown. The

results of the treatment of the experimental data for the systems HCl solution-phenol-benzene and phenol-chlorobenzene are presented in Fig.5 and 6 in the form of the dependences of the total extraction coefficients on the continuous phase rate.
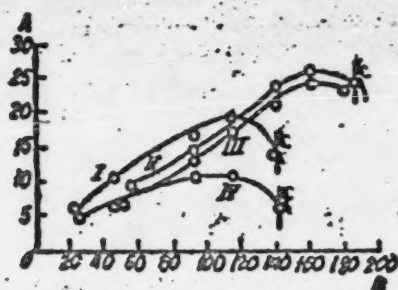
Fig.4. Effect of continuous phase rate on the extraction coefficient for the system water-acetic acid-benzene.
A — K(in kg-mole/m^3·hour·kg-mole/m^3); B — continuous phase rate.
V_c (in cm^3/min). I, IV — benzene dispersions; II, III — water dispersions. V_d(in cm^3/min):
I — 115; II — 92; III — 115; IV — 70; C — flooded.
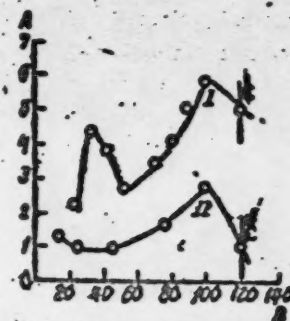
Fig.5. Effect of continuous phase rate on the extraction coefficient for the system HCl solution-phenol-benzene.
A — K_O (in kg-mole/m^3·hour ·kg-mole/m^3); B — continuous phase rate V_c (in cm^3/min). I — benzene dispersion; V_d — 55 cm^3/min; II HCl solution dispersions, V_d — 50 cm^3/min; C — flooded.
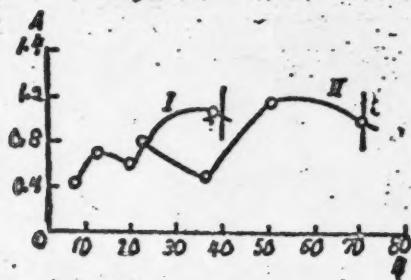
Fig.6. Effect of continuous phase rate on the extraction coefficient for the system HCl solution-phenol-chlorobenzene, HCl solution disperse phase.
A — K_O (in kg-mole/m^3·hour·kg-mole/m^3); B — continuous phase rate V_c(in cm^3/min). I — V_d = 25 cm^3/min; II — V_d 45 cm^3/min; C — flooded.
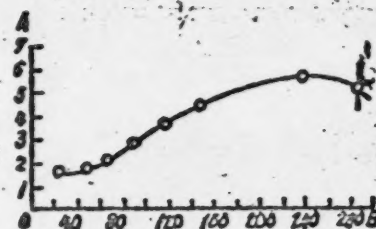
Fig.7. Effect of disperse phase rate on the extraction coefficient for systems HCl-solution-phenol-benzene, HCl solution-disperse phase, V_c = 55 cm^3/min.
A = K_O (in kg-mole/m^3·hour· kg-mole/m^3); B — disperse phase rate, V_d (in cm^3/min); C — flooded.

As emerges from these figures, at comparatively small rates of the disperse phase, the coefficients of extraction commence to increase, then they fall, attaining a minimum value of the rate for each system. Further increase of the disperse phase rate causes the extraction coefficient to increase and consequently the column then works more effectively.

The hydrodynamic conditions which secure the most efficient operation of the packed extraction column with maximum output, can evidently be defined as the optimum running conditions. The optimum hydrodynamic conditions are independent of whether the one liquid or another is used as the disperse phase. Thus, in Fig.4, the results of experiments using aqueous acetic acid solutions as continuous and disperse phases show that the maximum value of the extraction coefficient is reached in both cases at the same definite value of the continuous phase rate. The same thing emerges from experiments on extraction of phenol with benzene and chlorobenzene. These hydrodynamic conditions are those corresponding to emulsion formation.

The relative change of the maximum value of the extraction coefficient as a function of the directive phase employed, correlates as follows: it is expedient to select as directive liquid the one in which the solubility of the substance distributed between the phases is the largest. Thus, in Fig.8, the effect of changing the phase in the extraction of acetic acid from aqueous solution with benzene is shown. The solubility of acetic acid in water is higher than in benzene and the use of an aqueous solution of acetic acid as a disperse phase gives a value of the maximum extraction coefficient larger by 25%.

Fig.8. Influence of the change of phase on the extraction coefficient and limits of loading for the system water-acetic acid-benzene.
$A = K$(in kg-mole/hour m^3 · kg-mole/m^3): B — continuous phase rate V_c (in cm^3/min) I — benzene disperse phase, V_d — 115 cm^3/min; II — water disperse phase, V_d — 115 cm^3/min; C — flooded.
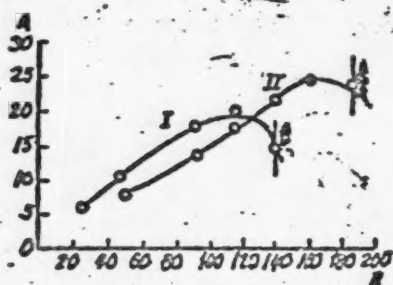
A still larger effect is obtained in the extraction of phenol from HCl solutions with benzene using benzene as the disperse phase (Fig.5). The lowering of the limits of loading in this case (Fig.8) can be explained, on the basis of the earlier hydrodynamic investigations and the generalized graphs obtained there [1], by the lowering of the optimum value of w_c with increase in the specific gravity of the continuous phase γ_c of the same system.

The effect of the change in the disperse phase rate at constant continuous phase rate was studied on the system HCl solution-phenol-benzene.

From a comparison of the experiments with the change of the continuous phase rate with those involving change in the disperse phase rate, the following conclusions emerge:

By maintaining the continuous phase rate constant at the lower limit — the flooding limit — the limiting loading of the disperse phase can be considerably increased. This is in complete agreement with the results of the hydrodynamic analysis of the working of extraction columns. From an analysis of the generalized graphs [1], it follows that the relative increase of the disperse phase rate at fairly small continuous phase rates enables the loading limit of the column to be increased in the disperse phase and, consequently, enables the throughput of the column with this liquid to be raised.

Such relations of the phase rates lead to relatively high extraction coefficients since the continuous phase becomes more saturated with the dissolved phase.

b) Effect of the physical properties of the liquids. It would be expected that the physical properties of the system would exert a considerable effect on the process of mass transfer, because the loading limit of the column depends on them.

If the system comprises liquids whose densities only differ slightly, then the limiting flow rate will be considerably lowered, as a result of which the amount of turbulence in the boundary films will be small. Hence with fairly close values of the distribution coefficients of two systems it would be expected that the system with the liquids differing less in density would give the smaller value of the extraction coefficient.

In Fig.9 is given the effect of the disperse phase rate on the extraction coefficient for the systems HCl solution-phenol-benzene and phenol-chlorobenzene, for which the distribution coefficients differ only by a small amount (2.91 and 4.43) within the limits of the operating concentrations. The densities of these systems differ considerably: for the first it is 203 kg/m^3, while for the second it is 20 kg/m^3; as a result of which, as the figure shows, there is a considerable lowering of the extraction coefficient of the system HCl solution-phenol-chlorobenzene (by comparison with the other system).

The surface tensions in the systems exert a similar effect: thus, the higher value of the surface tension in system I (73.6 dynes/cm) by comparison with that for system II (14.39 dynes/cm) causes larger drops to be formed, which become entrained in the packing, and thereby impede the movement of the liquids and impair the conditions for mass transfer.

c) Effect of the packing on the process of mass transfer. The effect of the packing on the mass transfer is shown in Fig.10, in which are shown the results of our experiments on the extraction of acetic acid from aqueous solution, carried out with packings 6.62 x 6.70 mm($\sim$1/4") with those obtained by Sherwood for the same system, using packings of 1/2" size. The change in the effectiveness of the packings is shown as the dependence of the integral height of the packing on the continuous phase rate introducing corrections into Sherwood's data [3] for the ratio of the effective volumes of the packings as between Sherwood's experiments and our own.

The following conclusion can be drawn from Fig. 10: (1) The character of the change of the effective working of the extraction column with change of the continuous phase rate remains the same for different sizes of packing, but in Sherwood's experiments emulsification was not established and the maximum effectiveness was obtained only at small flow rates; and (2) the integral packing height increases with increase in the size of the packing unit, and the effectiveness of the extraction column is correspondingly lowered.
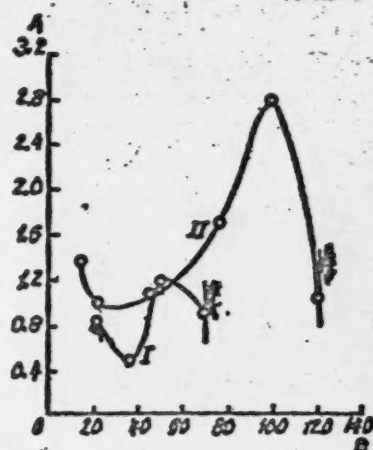

Fig.9. Effect of the physical properties of the liquids on the coefficient of extraction and the limits of loading. A — K_O (in kg-mole/m^3·hour·kg-mole/m^3); B — rate of continuous phase, V_c (in cm^3/min); C — flooded. I — HCl solution-phenol-chlorobenzene, V_d — 46 cm^3/min; II — HCl solution-phenol-benzene, V_d — 50 cm^3/min.

DISCUSSION OF THE RESULTS

It is of the greatest practical interest to obtain a generalized dependence of the effectiveness of operation of the extraction columns at the limits of optimum operation, on those hydrodynamic factors which determine the existence of such conditions.

From the analysis of the hydrodynamic basis of the operation of a packed extraction column it follows that the dimensionless ratio V_c/V_d determines the limiting column loading; here V_c and V_d are the rates of the continuous and disperse phases in m^3/m^2 hour. Since the optimum working conditions for the column are close to the limit of loading, any evaluation of the experimental data, corresponding to the optimum, should be made in terms of the dimensionless ratio V_c/V_d.

The Prandtl diffusional criterion, taking the rate of the continuous phase as the fixed one, may be expressed in the form:

$$P_r = \frac{\mu_c}{\rho_c D_d}, \qquad (7)$$

where μ_c is the viscosity of the continuous phase (in $kg \cdot sec/m^2$); ρ_c is the density of the continuous phase ($kg \cdot sec/m^4$); D_d is the diffusion coefficient (m^2/sec).

If the effectiveness of operation of a packed extraction column is expressed as the ratio h_i/d_e where h_i is the integral packing height and d_e is the equivalent diameter of the packing, then the change in the operational efficiency of the column for the optimum conditions may be expressed as follows:

$$h_i/d_e = f\left(\frac{V_c}{V_d}, \quad \frac{\mu_c}{\rho_c D_d}\right). \qquad (8)$$

Fig. 10. Effect of the size of the packing on the integral height.

A - h_i (in mm); B - continuous phase rate, V_c (in cm^3/min). I - V_d = 61.8 ml/min., 1/2" packings; II - V_d = 70 cm^3/min, 1/4" packings.

By working out the experimental data on extraction for different systems and packings under optimum running condition (points corresponding to the maxima in Figs. 4-7) in the functional form presented above, the graph shown in Fig. 11 may be constructed.

A straight line is obtained, around which the experimental points are grouped: this line has a slope of 1/3.

The equation may be written in the form:

$$h_i/d_e = 1.15 \frac{1}{\left(\dfrac{V_c}{V_d}\right)\dfrac{1}{3}} \cdot P_r^{2/3} \qquad (9)$$

The generalization obtained may be taken as satisfactory over a wide range of physical properties of the systems investigated and for different sizes of packing.

Comparison of the continuous phase rates, corresponding to optimum running conditions, with the rates determined from the hydrodynamic graph enable a more

definite connection between the hydrodynamics and the mass transfer in packed extraction columns to be extablished.

For given values of V_c and V_d on the hydrodynamic graph [1] there is a linear continuous phase rate corresponding to the flooded state of the column; by lowering these values about 20%, the necessary diameter of the extractor is obtained.

With the aid of Equation 9, for the same values of V_c and V_d, the value of the integral height of packing is determined and thereby the necessary packing height for all columns.
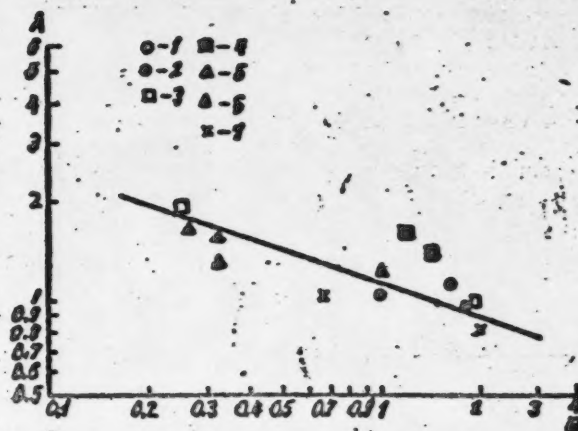
Fig. 11. Generalization of the experimental data for optimum running conditions.

$$A - h_1/d_e/F_r^{2/3} \; ; \; B - V_c/V_d.$$

1 - Water-acetic acid-benzene
2 - HCl solution-phenol-benzene   } Author's data,
3 - Benzene-phenol-HCl solution   packing
4 - Chlorobenzene-phenol-HCl solution   6.6 x 6.7 mm
5 - Water-acetic acid-benzene, packing
   12.7 x 12.7 mm   } Sherwood's
6 - Benzene-acetic acid-water ⎰packing   data
7 - Water-acetic acid-benzene ⎱25.4 x 25.4 mm

SUMMARY

1. The optimum running conditions of packed extraction columns have been established, these being those of emulsification, in which the most effective mass transfer is attained.

2. The relation between the hydrodynamic regime and the operational effectiveness of the column has been demonstrated.

3. The quantitative relationship between mass transfer and the hydrodynamic factors under the conditions of optimum running have been established.

4. A scheme for the determination of the basic dimensions of packed extraction columns operating under the optimum conditions, has been indicated.

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[1] V. V. Kafarov and M. A. Planovskaya, Hydrodynamics of packed extraction columns. J. Appl. Chem. 24, 6 (1951).[1]

[2] A. Seidell, Solubilities of inorganic and organic compounds, 2, 1007 (1928).

[3] T. K. Sherwood, I. E. Evans., I. V. A. Longcor, Ind. Eng. Chem., 31, 1144 (1939).

[1] See Consultants Bureau English Translation, p. 699.

ROLE OF THE STATE OF AGGREGATION OF DIFFICULTLY SOLUBLE OXIDES

IN THEIR REDUCTION BY CARBON IN INDUSTRIAL FURNACES

A. S. Mikulinsky

Ural Chemical Research Institute (UNIKHIM)

In the present paper an attempt is made to examine some of the general statements which express the conditions for obtaining metals or carbides in the reduction of oxides by carbon, in electrical furnaces of the type used for carbides, ferro alloys, and those similar to them.

In the first part of the paper the primary and secondary processes which are most likely to occur in a furnace are discussed. It is natural that in each particular furnace installation only some of these are of predominant importance. In the later parts the ideas which in some measure may facilitate the determination of these predominant processes are discussed.

Processes occurring in industrial furnaces

Primary processes. As an example, the well known case of the reduction of a metal oxide with carbon, producing either a metal or the carbide, is taken:

$$oxide + carbon \rightleftharpoons carbide + carbon\ monoxide$$

i.e.,

$$\frac{k}{m} Me_mO_n + \left(1 + \frac{kn}{m}\right) C \rightleftharpoons kMeiC + \frac{kn}{m} CO; \tag{1}$$

$$oxide + carbon \rightleftharpoons metal + carbon\ monoxide$$

i.e.,

$$Me_mO_n + nC \rightleftharpoons mMe + nCO \tag{2}$$
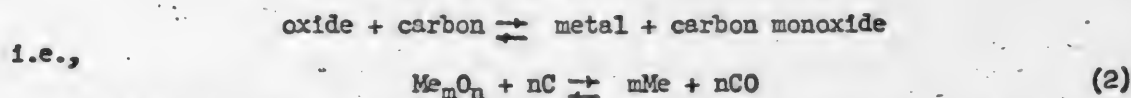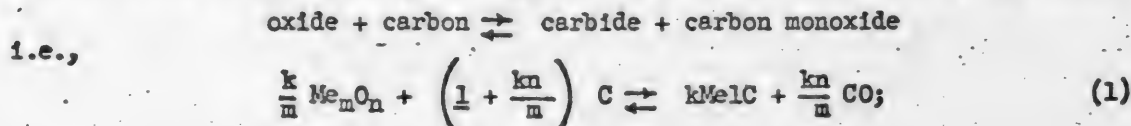
In a number of operations reactions occur, as a result of which the valency of the metal in its oxide is reduced:

$$Me_mO_n + (n - m)C \rightleftharpoons mMeO + (n - m) CO, \tag{3}$$

for example

$$SiO_2 + C \rightleftharpoons SiO + CO.$$
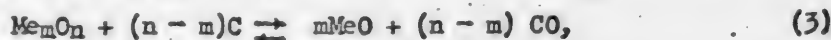
Attention should also be paid to the reactions in which the lower oxide of a metal arises as a result of dissociation:

$$2Me_mO_n \rightleftharpoons 2mMeO + (n - m) O_2. \tag{4}$$
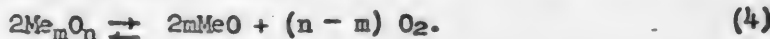
As an example the reaction

$$2SiO_2 \rightleftharpoons 2SiO + O_2$$
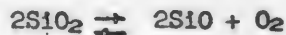
may be adduced.

This latter reaction was indicated by Shedroitsky [1], and independently Reaction (4) in its general form was introduced by the author [2]. Calculations using provisional chemical constants for silicon monoxide, given by Geld [3] showed that the sum of the partial pressures of silicon monoxide and oxygen over silica attains 1 atm at a very high temperature – 2800°; at 2000°

it is only 1 mm Hg. None the less, the possibility of the dissociation of silica must not be neglected. The cause of this is the close association of the products of Reaction (4) with carbon and the presence in the furnaces under known conditions of regions at temperatures exceeding the normal.

In furnaces, the oxides and reaction products also volatilize:

$$\left.\begin{array}{l} MeO_{s,1} \rightleftarrows MeO_{vap}; \\ Me_{s,1} \rightleftarrows Me_{vap}; \\ MeC_{s,1} \rightleftarrows MeC_{vap}. \end{array}\right\} \quad (5)$$

Maximenko has indicated that the reduction of the oxides of silicon and calcium precedes their evaporation [4]. This process, probably, is of importance for the preparation of silicon or its alloys. However, the author and Maron [2] have shown that this reaction cannot, for a number of reasons, be a predominant one in the manufacture of calcium carbide.

In comparing the material and thermal balances of open hearth furnaces, it is usual to take into account the combustion of carbon, at the surface of the furnace, with the oxygen of the air to form carbon monoxide and carbon dioxide. The author has shown that in furnaces of the carbide type, air penetrates deep into the charge. As a result of this the following reactions must be taken into account:

$$\left.\begin{array}{l} C + O_2 = CO_2, \\ 2C + O_2 = 2CO, \end{array}\right\} \quad (6)$$
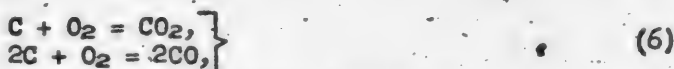
which result in a further consumption of carbonaceous substance.

Secondary processes. Oxides in certain processes may be reduced by gaseous reagents.

Experiments by Geld and the author in 1939-1940 showed the possibility of such reduction of magnesium. The experiments were carried out at 1500-1700° in an atmosphere of hydrogen. Briquets of magnesia were inserted into a carbon tube so as to be out of contact with the walls of the tube. The reduction of magnesia was a consequence of its interaction with hydrogen and hydrocarbons formed by reaction between the walls of the furnace and water vapor adsorbed upon it.

It may be supposed that such hydrocarbons are formed in a number of industrial smelting furnaces and reduction can follow the scheme:

$$oxide + hydrocarbon \rightleftarrows metal\ (or\ carbide) +$$
$$+ carbon\ monoxide + water\ vapor. \quad (7)$$
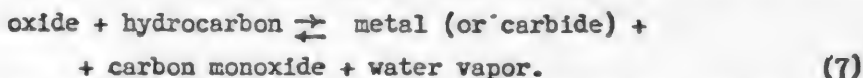
The possibility of the reduction of comparatively easily reduced oxides, by carbon monoxide, must be borne in mind:

$$MeO + CO = Me + CO_2. \quad (7a)$$
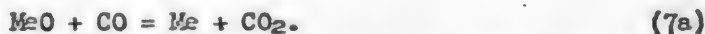
For example, in the manufacture of aluminous cements part of the ferric oxide in the bauxite can be reduced by this scheme.

The volatile oxides formed in furnaces can be reduced by one of the following reactions:

$$CaO_{vap} + C = CaC_2 + CO;$$
$$SiO + C = SiC + CO;$$
$$SiO + C = Si + CO.$$
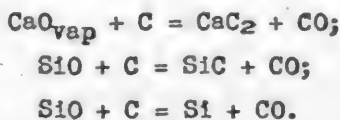
The interaction of oxide with metal must be kept in mind:

oxide of higher valency + metal $\rightleftharpoons$ oxide of lower valency

i.e.,

$$Me_mO_n + (n - m)\, Me \rightleftharpoons nMeO; \tag{8}$$
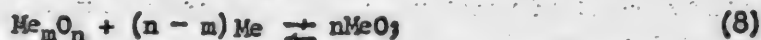
oxide of metal of lower valency + other metal $\rightleftharpoons$ oxide of other metal + metal. $\tag{9}$

An example of Reaction (8) is

$$SiO_2 + Si \rightleftharpoons 2SiO,$$
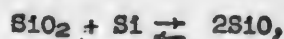
which, as Geld has shown, is of great importance in the manufacture of silicon and its alloys.

An example of reaction (9) is:

$$SiO_{vap} + Fe = FeO + Si_{(Fe)}.$$
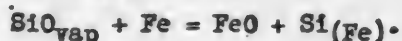
The latter reaction, which is exothermic, probably occurs in the manufacture of ferrosilicon from quartz, carbon and iron. The ferric oxide formed is reduced by the carbon monoxide with formation of carbon dioxide which, in its turn, is reduced by carbon to carbon monoxide. Thus the introduction of iron into the charge involves a sharp reduction of the expenditure of material and electrical energy.

In the high temperature zones of the furnace, conditions may be created in which dissociation of a number of initial or final products occurs. It is generally known, for example, that in furnaces for the manufacture of silicon carbide silicon volatilizes from the carbide around the core, and graphite is deposited. This suggests that in calcium carbide furnaces a similar dissociation of the product occurs.

Thus, in electrothermal furnaces, reactions of the type:

carbide $\rightleftharpoons$ metal + carbon   occur,

i.e.

$$Me_kC_1 \rightleftharpoons kMe + 1C. \tag{10}$$

Carbides or metals, obtained by reactions (1) and (2), in their turn interact with oxides as follows:

oxide + carbide $\rightleftharpoons$ metal + carbon monoxide

i.e.

$$Me_mO_n + \frac{n}{1}\, Me_kC_1 \rightleftharpoons \left(m + \frac{kn}{1}\right) Me + nCO. \tag{11}$$
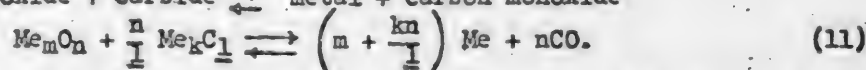
The occurrence of such a type of reaction between oxides and carbides of calcium or aluminum, or silicon, has been mentioned by a number of authors [6-9].

To this type of reaction also belong those where the non-oxygen component in the oxide has a lower valency, for example in the reaction

$$SiO + SiC = 2Si + CO. \tag{11a}$$

The author [2] has reported on the occurrence of reaction (11a) in general, and Shedrovitsky [1] and Dashevsky and Khitrik [9] in its application to the system silica-carbon. In the latter work there is a considerable bibliography.

In smelting furnaces there is a widespread interaction of the oxide of one metal with the carbide of the other. This is illustrated by the example of the decomposition of aluminum carbide with silica, which Rapaport [10] has

given. The possibility of a reaction of the type:

$$Al_4C_3 + 3SiO = 4Al \cdot 3Si + 3CO$$
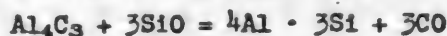
must also be borne in mind: as a result of which the alloy should contain 48% of silicon; in actual fact a low-carbon alloy containing 30% of silicon could not be obtained. Such a result means that, in the reduction of alumina with carbon and without addition of silicon containing materials, 40-50% of metallic aluminum is formed in addition to the metal carbide.

It is known that silicon or its oxide is frequently chosen as a means for transforming the bound carbon in metals. This can be explained by the fact that in many cases silicides are formed with a considerable heat effect and hence are stable even at high temperatures. As an example calcium silicide may be adduced: it is stable at temperatures around 1800°. The author maintained calcium silicide containing about 30% of calcium at 1700° and 1 mm. Only a small portion of the latter distilled off from the silicide.

It should further be remembered that the low ratio of the atomic weight of silicon to its valency $(28/7 = 4)$ makes it possible to obtain low-carbon alloys with comparatively small weight contents of silicon.

There are references also in the literature to the reaction:

$$\text{carbide of one metal + other metal} \rightleftarrows \text{intermetallic}$$

$$\text{compound + carbon.} \tag{12}$$
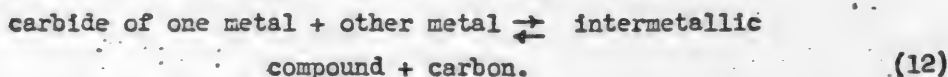
From the course of reaction:

$$\text{carbide + Si} \rightleftarrows \text{silicide (or alloy) + carbon}$$

during the manufacture of silicochromium, it emerges that the solubility of carbon in falls as the silicon content increases [11].

In conclusion we should say that study will both change and extend the list of these processes.

The ratio of the quantity of vaporized substance formed in the conversion to the intended product

It is known that the products of a number of reactions, in particular Reactions (3), (4), and (5), are present in the vapor state in the lower part of the furnace. A part of the volatile substance, formed for example in Reactions (1), (9), and (11), encountering the initial substance, forms fresh products, which are predominantly those aimed at. The other part of the vaporized substance is not converted to the products intended, and it rises to the cold part of the furnace, where it condenses on particles of the charge. A third part of the vapor leaves the furnace, forming a finely divided dust at its throat. The condensation of substance does not mean that any is lost, but there is a transfer of heat from the lower to the upper zones of the furnace, accompanied by an elevation of the temperature of the latter. It should be taken as desirable that the vaporized substances formed in the lower part of the furnace should be converted to the desired end products, and should not escape to the upper zones, where they can condense.

The intermediate formation of vaporized substance causes the particles of the charge to stick together, due to precipitation of the condensate upon them, or due to the occurrence of the reaction on their adjacent surfaces. The latter may happen, for example, in the reduction of silica, with carbon, to silicon

or one of its alloys, in cases where the intermediate compound— carborundum— does not participate in Reaction (11).

Let us designate the quantity of volatile substance formed per unit of time by A, and the quantity of vaporized substance converted to the desired end product, as B. In the reduction process, $A > B$, the value of $A - B$ in many furnace installations is so great that it constitutes one of the most important sources of loss of material and energy. To illustrate this we recall that raising the silicon content in ferrosilicon involves a considerable increase in the specific consumption of electrical energy and quartz, due to the increase in the quantity of vaporized silicon-containing substance formed.

The quantity of vaporized substance, not converted to the end product, can be small in relation to the quantity of all the initial substance, however it frequently represents an overwhelming part of the loss of substance, which in its turn gives rise to the principal loss of electrical energy. This indicates the need to increase B and diminish A.

Increase of B is attained by increasing the time of contact of the vapor components with the initial solid substance, mainly carbon. Diminishing A is attained by diminishing the rate of flow of gases or vapors, by increasing the cross sectional area of the furnace[1] through which the gas streams out. At the same time an improvement of the heat exchange between the hot gases and the cold charge is produced With more complete heat exchange the temperature of the gases in the furnace falls and this in turn lowers their flow rate. These two favorable factors improve the conditions for condensation and the retention of the fine dust particles of the condensate. Another favorable factor appears to be an extension of the zone of interaction of the products, which is attained by deeper immersion of the electrodes. In certain smeltings, for instance in the production of silicon, the necessity of using wood charcoal as well as coke as carbonaceous substance emerges; this because of the higher sorptive properties of charcoal for the vapors of SiO_2, SiO, and Si.

Generalizing what has been said, we note that to increase the degree of completeness of conversion of the vapor intermediate substances to the desired end products requires that for each element of volume of these substances there shall be a sufficient space in the furnace, and a high enough temperature, for this conversion to proceed most intensively. Noting that the quantity of vapor substances formed, other things being equal, is proportional to the power consumption of the furnace, we formulated the principle of energy concentration [2], which determines in the main the lower temperature limit of the furnace.

From what has been said the following can be deduced:

1. In the study of the index of operation of a furnace it is not only the processes predominating in the furnace which are of importance, but also the processes determining the magnitude of $A - B$. This must be borne in mind for the exploitation and the determination of the parameters of the furnaces.

2. In the study, under laboratory conditions, of processes proceeding in shaft smelting furnaces, the effect of the upper filtering layer of charge must be considered relative to the formation of intermediate products as a result of processes proceeding in the lower zones. For this purpose the refractory tube with the charge should be inserted into the furnace in such a way that the lower

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[1] Extension of the effective cross sectional area of the furnace and increase of the depth of the electrodes depends on the electrical parameters. This is discussed in another paper [2].

layer is at the temperature of the process being studied, and the upper layer is at a lower temperature – in the majority of cases 200-600°.

Upper temperature limit in the furnace

According to a number of authors, in shaft smelting furnaces of the type of the blast furnace and others similar to it, the temperature in the charge is determined by the fusion temperature either of the slag, or of the ore. In the literature, however, arguments are not presented on the basis of which preferences for one or another temperature may be founded. Apart from this it has been shown [2] that the maximum temperature in furnaces of the blast furnace type is in general determined not by the fusibility, but by the fluidity of the slags or ore.

It has also been observed [2] that the criterion of the fluidity of the slags or ores is not a general one for determining the maximum temperature in a number of shaft furnaces, particularly electrical ones.

In this connection the author advanced the general formulation of the principle of the maximum temperature set out below:

1. In shaft furnaces – fuel fired or electrical – in which physical or chemical processes are in progress, accompanied by the conversion of all the initial substances to the liquid or gaseous condition, this change in the state of the charge is the cause of its aggregation.

In these furnaces, in the absence of any check on the aggregation of the charge, a maximum temperature is established which is sufficient to convert all the initial substance to a sufficiently liquid state. In furnaces where products of insufficient liquidity are formed, the maximum temperature of the substances exceeds the temperature of fusion by the increase in temperature of the liquid when sinking through the charge. When the aggregation of the charge is checked, the temperature of the smelting furnace rises.

The second item of the principle may be expressed in the following form:

2. The maximum temperature in these furnaces is that which is sufficient for the occurrence of that physical or chemical process which is necessary to get complete aggregation of all the charge.

To illustrate the application of the principle, some examples are presented, which together with the previous partial exposition constitutes a simultaneous indication of its correctness and generality.

a) On the basis of a number of factors and considerations, which are presented in the works of Maximenko [4], Markovnikov [12], the author and Maron, Geld and others, we suggest that the following scheme can be advanced for the course of the processes involved in carbide formation in industrial electric smelting furnaces.

After starting the furnace, or in normal running after complete discharge of the liquid carbide, or on overheating the charge, carbide is formed as a consequence of the contact of the fine solid particles of the charge and the evaporated lime with carbon. The "maximum" temperature in the furnaces rises to the value necessary for the occurrence of these high temperature processes. However, after the formation of some quantity of carbide and its interaction with the lime, a liquid phase appears and later the normal process of carbide formation proceeds, involving the participation of the liquid phase which requires a higher temperature; the latter corresponds to a new "maximum" temperature.

Lime dissolves in the carbides obtained, interacts with the carbon, and forms calcium carbide. Additional portions of lime dissolve in the saturated solution of calcium carbide in the calcium carbide-lime system; then calcium carbide is formed afresh, etc.

It is known that the CaC_2 content in the carbide melt obtained is not that corresponding to the eutectic point, which lies at 70% carbide, but is 75-85%. This is because the carbonaceous material is introduced into the charge in quantity necessary for obtaining a product having this latter composition. As long as all the carbon, making allowance for what gets burnt, does not enter into reaction with the lime, the sinking of the charge is checked.

b) The reduction by carbon of the liquid pure silica, if it occurs at all, does so only to a very small extent, as a consequence of the extremely high viscosity of the liquid silica and because liquid silica only wets carbon very slightly. Only quartzite, contained as an impurity, can form inclusions of comparatively fluid and reactive liquid. The reduction of pure silica occurs by interaction of silica with silicon, or by its evaporation, or dissociation according to Equations (8), (5), and (4). Furthermore the silicon monoxide vapor interacts with carbon, forming carborundum, which reduces the silicon monoxide vapor to the element in accordance with Reactions (11) and (11a). With iron present in the charge, as in the production of ferrosilicon, it is extremely probable that the reduction of silicon monoxide occurs with formation of ferrosilicon and ferric oxide according to Reaction (9).

c) There are shaft furnaces in which the cause of the aggregation of the charge is not its entire conversion to the liquid state, but to the vapor condition. For example in the reduction of magnesia by carbon, carbon monoxide is formed along with vaporized magnesium, which is condensed outside the furnace in a stream of hydrogen.

From these examples it is seen that in shaft furnaces with liquid or vapor products, processes occur which ensure the mobility of the charge at the lowest temperature.

Actually, in the furnace conditions for obtaining calcium carbide, the cause of the aggregation of the charge is not the melting of calcium oxide or of carbon, which occur at temperatures of 2500 and 3900° respectively, nor is it the fusion of the product of the process – calcium carbide, since the fusion point of this depends on the ratio between the oxide and calcium carbide in the charge, which in turn depends on the temperature in the furnace. Evidently the cause is the chemical process of obtaining the liquid carbide from lime and carbon, which proceeds at about 1800°. This corresponds to the "maximum" temperature of the furnace.

In the production of silicon the cause of the aggregation of the charge is not the fusion of quartz, which is not associated with the production of silicon and, consequently, not associated either with the conversion of the charge to the liquid state nor is it due to the fusion of the other component of the charge – carbon, nor with the fusion of silicon itself. It is evident that in the production of silicon or of its alloys the "maximum" temperature in the furnace is equal to "minimum" temperature which is sufficient for the formation of the silicon from the charge, since its formation leads to the aggregation of the charge.

The aggregation of the charge in the production of magnesium by the carbothermal method is not conditioned by the fusion either of the initial magnesia or carbon, nor of the products of the reaction – magnesium and carbon monoxide: they do not pass over into the liquid state in the furnace. The aggregation is

achieved at a " minimum" temperature necessary for the occurrence of the reducing process, as a result of which the whole charge is converted to the vapor condition.

There are, however, a number of processes which are carried out in furnaces at " maximum" temperatures, corresponding to the fusion temperature of the slag. To this class belongs the production of pig iron, phosphorus, and other products in shaft furnaces, where the slag is sufficiently fluid (i.e., has a viscosity of not higher than 2-7 poises). The " maximum" temperature may be close to the temperature of fusion of the ore (including the ferric oxide which cannot be reduced by the flue gases) in cases where this temperature is below the fusion temperature of the slag. For both the cases indicated above the criterion of fluidity of the slag or of the ore reflects a partial case of the principle of maximum temperature.

The examples quoted show the following.

In the high temperature zone of shaft furnaces, in which the aggregation of the charge is realized as a result of the change of the state of aggregation of the whole charge, importance attaches to that process which ensures the aggregation of the charge at the minimum temperature. This minimum temperature is at the same time the maximum temperature of the furnace.

It is necessary to add some explanations to the formulation given.

1) The principle of the realization of aggregation of the whole charge to the fluid state accords with the fact that after the fusion of one of the components of the charge an additional process of interaction of the liquid substance with the other solid substances in the charge may occur.

This corresponds, for example, to the fact that the primary slag reacts with the carbon in the blast furnace.

2) In a series of cases the effect of attraction between the solid particles and the liquid adhering to it, should be evident. This may be characterized by the work of adhesion W_{sl}. It increases in unison with the surface tension at the liquid-gas boundary $\gamma_{l.g.}$ and with increase of the wettability of the solid particles by the liquid [14]. It is known that many metals have a relatively large $\gamma_{l.g.}$ — about 600-1200 dynes/cm [15], and wet certain solids extremely well. From this it could be concluded that in a number of cases a process involving the participation of the liquid metal may occur, in accordance with, for instance, Equations (8) and (9), in spite of the small viscosity of the metals.

In the investigation of the interaction between iron turnings and pieces of quartz and coke in a laboratory furnace with its lower part at 1800° and the upper part at 500°, beads of different composition, containing iron and silicon, were observed on the pieces of quartz.

When the pieces of iron were replaced by pieces of aluminum, keeping the conditions of the experiments otherwise the same, and introducing enough aluminum to get an aluminum silicide with 35% of aluminum, metallic beads were obtained on the solid part of the charge, these beads containing 3% of Al. In this case, apparently, although the rate at which the metal trickled down was slower, the time of contact of the liquid aluminum with the quartz was insufficient to reduce the latter completely.

It follows that the fluidity mentioned in the principle, is determined for each substance not only by the viscosity, but also by the work of adhesion.

3) As is known, in shaft furnaces, in particular in ore smelting furnaces, encrustation and arresting of the aggregation of the charge occurs. As a

consequence of this, as Maximenko [4] indicated, the temperature in ore smelting furnaces is raised. Those processes occur which are required in order to maintain a temperature higher than the "minimum". For example, in the production of calcium carbide, when incrustation is formed there is an intense evaporation of calcium oxide, dissociation of calcium carbide, etc. At the end of such processes the "maximum" temperature may go even higher, right up to the temperature determined by the heat balance of the furnace, similar to what occurs in the core of a furnace for obtaining carborundum in stages, when this process maintains its own temperature and the electrical energy entering the furnace is required only to balance the external heat losses.

When the aggregation of the charge is checked, as a result of the formation of "crusts", the "maximum" temperature in the furnace is still not controlled by the temperature of change of the state of aggregation, since the charge cannot fall into the high temperature zone, where it could undergo a change of state; the reduction of normally aggregated material requires the destruction of the crusts by mechanical means.

4) It is known from practical experience with electrothermal smelting furnaces that, with excess of certain components of the charge, in particular of carbon, overheating occurs [16]. The explanation of this can be given from the principle of maximum temperature. Actually, in shaft furnaces, usually some of the reagents have a fusion temperature or boiling point higher than the "minimum" temperature of the process of converting all the charge to the fluid state. To convert an excess of reagent to the fluid state frequently requires a higher temperature. For example, excess of carbon in the charge prevents its aggregation so long as the excess carbon is not burned away either by air which penetrates deep into the charge, or by the liquid products. When such a check on the aggregation is in operation the temperature in the furnace rises.

5) There is a basis for suggesting that in shaft furnaces, in particular in thermal or smelting furnaces, and especially in cases of working at higher voltages pockets are formed at higher temperatures than the average "maximum" temperature of the main bulk of the material in the furnace. It is known that at increased voltage arcing is increased and thereby vaporized silicon monoxide is formed in furnaces obtaining phosphorus from phosphorites, carbon and quartz.

In ore-smelting furnaces, when, on any particular side of the lower electrode, there are regions of higher electrical conductivity, there arise between these regions and electrode the so-called shot holes — arcs which cause local overheating. In the given case the local conversion of the charge to the fluid state does not induce an aggregation of the charge, since the neighboring portions of the charge, not converted to the fluid state, prevent the aggregation in the same way as aggregation is prevented among particulate material in bunkers with comparatively narrow openings. A negative effect of the local overheating on processes which involve the participation of vaporized substances appears to be that such overheating causes a liberation of vapor in an extremely small section. The electrodes of the furnace prevent the spreading of this vapor across a section sufficient to cause all the vapor to be converted to the desired end product.

6) In so far as, in shaft furnaces with aggregation of the charge basically due to a change in the state of aggregation, conditions exist for raising the temperature of the ore above the "maximum", the essence of the principle is not that in corresponding furnaces the upper temperature levels are established automatically, but that there is the possibility of this happening. This possibility becomes a certainty when the causes preventing the aggregation of the charge are removed, for example when local overheating, incrustations and excess of carbon in the charge are eliminated.

It follows also from these facts, on the other hand, that in those cases where it is useful, it is possible somewhat to exceed the "maximum" temperature by artificial prevention of aggregation of the charge. Thus in those cases, phenomena such as formation of incrustations or introduction of excess of the components of the charge, become useful instead of detrimental.

7) The principle of maximum temperature is correct only for a definite class of furnace process, namely those where the temperature of the process designated by t_{pr}, and the temperature at which a sufficient fluidity of the whole charge is attained, designated by t_f, are equal, i.e., where $t_{pr} = t_f$. The importance of this equality suggests it as a basis for classification of furnaces.

In the class where $t_{pr} = t_f$, in the electrothermal field, furnaces are to be found in which a number of ferro-alloys are produced, in particular: ferrosilicon, carbon-containing ferrochromium, ferromanganese and others, calcium carbide, normal corundum, silicon, cast iron and others; those in which the chlorination of magnesium in the presence of carbon is carried out; those in which phosphorus, carbon disulfide, zinc, magnesium (carbothermal method), are produced. To this class also belong certain fuel-fired furnaces such as: shaft furnaces for the production of cast-iron, copper, lead, sodium sulfide, etc. The common characteristic of the furnaces enumerated is that the zone of highest temperature is below or above the layer of alloy; above this zone there is a layer of charge, the temperature of which diminishes in the direction of the throat. In electric furnaces, this is achieved by immersing the electrodes deeply into the charge.

The equality indicated above is attained in furnaces where the predominant process is the distillation or sublimation of metals, which also causes a transfer of the initial metal to the fluid condition. None the less, here the zone of highest temperature is not located in the very lowest working space of the furnace, since it is impossible in setting up these furnaces to immerse the electrodes deeply, as a result of which the original metal is a vehicle of the first kind.

Thus, the class of furnace distinguished by the equality $t_{pr} = t_f$, needs to be divided into two groups, the first of which, apart from this quality, is characterized also by a disposition of the high temperature zones below the layer of solid charge.

The second class is constituted by furnaces where $t_{pr} > t_f$. To this class, in particular, belong the reverberatory furnaces for the production or refining of ferrous and light metals.

In the third class are to be found furnaces characterized by the inequality $t_{pr} < t_f$. This class can be divided into two groups: to the first belong furnaces in which, as a result of technological processes, the primary particles of material do not stick together and thus do not create a check on the mobility of the materials. In it should be included, for example, the calcination of particulate carbonaceous substances in electric furnaces or the roasting of limestone or magnesite in fuel-fired furnaces. The aggregation of the charge here is realized by mechanical devices. The second group is characterized by the formation of non-mobile products without achieving continuous discharge from the furnace. Furnaces which approximate to this group appear to be those for the production of carborundum, calcium cyanamide, graphited electrodes and for such processes, which as a rule are carried out in batch furnaces.

From what has been said, it follows that the construction of furnaces is

essentially determined by the nature of the movement of the initial and final substance in it. This movement depends to a considerable degree on the relationship of t_{pr} and t_f. Hence it should lie at the basis of a classification of furnace production.

For electrothermal production, the classification outlined is more natural than the one based on the indication of the predominant current, flowing through the arc or the solid charge. This latter classification embraces in one group furnaces of different kinds of construction: for example, furnaces for the production of electro steel and ferrosilicon are included in the same group with those for the production of phosphorus, carborundum and graphited electrodes and others. An indication of the prevailing current is less important than an indication of the movement of the charge, but may, however, be useful for the classification of furnaces inside the classes.

It should be noted that the relation of this or that electrothermal production to this or that group is temporary. In a number of cases, there may be found such conditions as would permit the transfer of a given production from one group to another, thus securing a better index for it. To achieve this transfer in an intelligent manner, classification according to the most important characteristic is very important.

Kinetics of processes occurring in shaft furnaces and involving the formation of liquid products

As a result of the primary processes, vaporized or liquid substances are formed. The importance of the conversion of the primary vaporized substances to the desired product has already been mentioned. Here attempts will be made to assess the rate of interaction of solid and liquid substances on the basis of calculations carried out by the author.

The rate of reaction in shaft furnaces, expressed as a change of concentration of the desired substance in the time t, increases with increase in the diffusion coefficient D, whose value is inversely proportional to the viscosity τ, the free energy of the system F characterized by the equilibrium constant K_e the temperature function in the reaction zone of the furnace, designated $f(T)$, the work of adhesion $W_{s.l.}$, increase in which increases the time of contact of the liquid with the solid particle. and depends on change in diameter of the particle d, when the reaction proceeds on its surface. Consequently, we may write

$$dc = \frac{kf(T)K_t f(W_{s.l.})}{f(d)\eta} \cdot dt. \qquad (I)$$

Here k is a coefficient of proportionality. Assuming that to a first approximation the temperature in the reaction zone is constant, we express the viscosity, dimensions of the solid components and work of adhesion as functions of the concentration:

$$f(d) = f(c); \eta = \eta(c); W = W(c). \qquad (II)\ (III)\ (IV)$$

The substance formed trickles downwards, hence the rate of movement is a function of the viscosity: $v'(\eta)$.

Designating the height of the reaction zone by l, and the quantity of substance present at time t by x, then

$$\frac{dx}{dt} = v'(\eta)v''(W). \qquad (V)$$

From Equation V we have:

$$dt = \frac{dx}{\underline{v}'(\eta)\underline{v}''(W)}$$

From Equations (III) and (IV) we obtain, for the given temperature:

$$\underline{v}'(\eta)\underline{v}''(W) = \underline{v}'[\eta(c)]\,\underline{v}''\{W(c)\} = \underline{v}(c)W(c).$$

Consequently,

$$dt = \frac{dx}{\underline{v}(c)W(c)}$$

Inserting the value of $\underline{dt}$ in Equation (I) and using Equation (II) we obtain:

$$dc = \frac{k\underline{f}(T)K_e}{\underline{f}(c)\eta(c)W(c)\underline{v}(c)} \tag{VII}$$

After integrating, we obtain:

$$\int_0^c \eta(c)\,\underline{f}(c)W(c)dc = k\underline{f}(T)K_e \int_0^1 dx = kK_e\,\underline{f}(T)\underline{1}. \tag{VIII}$$

Equation (VIII) can be integrated since all the expressions within the integral are functions of the concentration of the end product. For numerical solutions, of course, the functional dependences involved in the equation should be determined by investigation. For a concrete system Equation (VIII) assumes a more simple form, since separate parts of the factors can be neglected. To refine the calculation, the concentrations in Equation (VIII) should be replaced by activities.

In shaft furnaces, where the charge aggregates as a result of physicochemical processes, as the liquid has a small viscosity, the magnitude of $\underline{v}$ from Equation (VIII) grows more rapidly with D after this. This is confirmed by the fact that when liquid products appear in shaft furnaces, the liquid has such a low viscosity that its rate of settling outstrips the rate of the succeeding processes, chemical and thermal. In general, at a constant value of the work of adhesion $\underline{W}$, there is some favorable interval of viscosity within which chemical processes proceed at the necessary speed; at higher viscosity, the rate of diffusion is small, and at low viscosity, the rate of settling of the liquid is extremely large.

SUMMARY

1. It has been shown that the processes of transformation of vaporized products to the end products should be taken as a first step in the determination of the furnace parameters and the analysis of the method of exploiting them.

2. The maximum temperatures in shaft furnaces are important both for converting vaporized products to end products, and for obtaining provisional products in liquid media.

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USE OF RECTANGULAR SYSTEMS OF COORDINATES FOR THE

CALCULATION OF MOIST PORTLAND CEMENT MIXTURES

M. I. Strelkov

Several means for the graphical calculation of Portland cement mixtures have been proposed.

For example in 1925, Orlov [1] described the calculation of mixtures from two materials, using a triangular diagram for the system $CaO-SiO_2-Al_2O_3$. In 1928 Grun and Kunze [2] published a method for calculating mixtures from two and three materials. Kind [3] in 1932, showed that mixtures can be calculated with the help of Grun and Kunze's diagrams, using the coefficients of saturation of alumina by lime introduced by them. Later, Okorokov [4], showed that such calculations can be executed very conveniently for given ratios of the mineralogical components in the clinker.

However, the graphical calculation of cement charges has not gained sufficiently wide popularity, since a number of important points remain untreated. For example, calculations taking account of the addition of fuel ash, which is extremely important in practice, have not been treated. Calculations have been carried out for materials previously reckoned as calcined substances. This has raised the need for reckoning the composition of mixtures on uncalcined material. All these calculations, requiring a great deal of time, deprive the graphical method of its basic advantage — rapidity. Apart from this, according to Grun and Kunze, it is impossible to make calculations for mixtures containing more than 3 raw materials. In their work on the question of representation of clinker by means of intercepts, they resorted to the method proposed by Lodochnikov [5]. However, they did not use Lodochnikov's method and in calculation indicated on the composition diagram the composition of the raw material and of the clinker produced by one point. As is known, in this case it is impossible to consider mixtures of four and more materials.

Thus the existing graphical methods of calculating cement mixtures leave much to be desired. The author has proposed a method [6] which eliminates all the difficulties mentioned. The theoretical basis of this method is presented below.

The raw materials used for the production of Portland cement, and likewise the clinker obtained from them are single-component materials. Usually their composition is expressed in weight percentages of oxides determined by chemical analysis. When the analysis has been carried out correctly, the sum of the oxides should theoretically add up to 100%.

Any similar material may be conventionally examined as a mixture of a different number of components, the composition of the material always being made in the following form:

$$\sum_{n=1}^{n=m} K_n = 100\%$$

where $\underline{K}$ = percentage composition in the mixture (in the material) of any component[1)]

[1)] In the rest of this paper, $\underline{x}$ and $\underline{y}$ will be used to denote the composition of the materials, expressed in percentages.

$\underline{n}$ = number of components, changing from unity up to the desired final positive number $\underline{m}$.

From what has been said it follows that, where the material consists of two components $\underline{x}$ and $\underline{y}$, we should have

$$y + \underline{x} = 100, \text{ or } y = 100 - \underline{x} \tag{1}$$

which is the equation of a straight line (BM, Fig. 1). This line intersects the axes $\underline{Ox}$, $\underline{Oy}$ in the points $\underline{D}$ and $\underline{b}$ with the coordinates $\underline{x} = 0$, $y = 100$ (point $\underline{D}$), and $\underline{x} = 100$, $y = 0$ (point $\underline{b}$). As a result of this an isoceles right angled triangle is obtained, $\underline{ODb}$.

Thus, any relation between $\underline{x}$ and $\underline{y}$, corresponding to the condition (1), i.e. any two-component material or mixture can be graphically represented by a point, lying on the line $\underline{BM}$, in particular, along a part of this line — the section $\underline{Db}$, being the hypotenuse of the right-angled triangle $\underline{ODb}$. The coordinates of these points will be determined by the values of $\underline{x}$ and $\underline{y}$. Thus, for example, the coordinates of the points $\underline{C_1}$, lying on the hypotenuse $\underline{Db}$, (Fig. 1) will be: the intercept $\underline{OC_0}$ — ordinate, and C_0C_1 — abscissa.

Consequently, the composition of the two-component mixtures is determined by the position on the diagram of the intercept C_0C_1. This intercept cuts off a length $\underline{OC}$ on the vertical axis, corresponding to the content of component $\underline{y}$ in the mixture; at the other end this line C_0C_1 (point $\underline{C}$), always lies on the line $\underline{BM}$, i.e. on the hypotenuse or on its prolongation. The length of the intercept C_0C_1 indicates the relative quantity of the component $\underline{X}$ in the mixture. Hence in accordance with the change in the proportions between the components in the material noted above (mixture) there will be a corresponding displacement of the points C_0 and C_1: the point C_0 along the vertical axis $\underline{Oy}$, and the point C_1 along the line $\underline{BM}$.
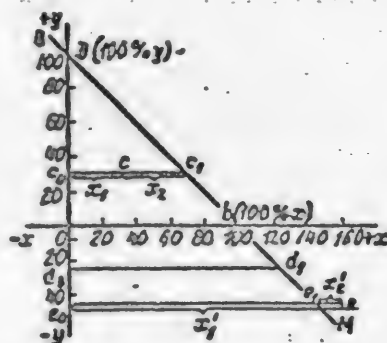
Fig. 1

When the point C_1 lies within the limit of the hypotenuse $\underline{Db}$, we have a real material in which both components are positive.

Usually in physical chemistry, those partial cases are used, selecting the intercept $\underline{Db}$ for representing the proportion of components in two-component systems. For graphical calculations, the case must also be considered where one of the components is larger than 100, and the other is negative. Only the condition that their sum should be equal to 100 (Equation 1) must be strictly complied with.

Thus, if $\underline{x} = 125$, then $y = -25$ (point d_1 on Fig. 1). Since this value corresponds to the equation of the straight line $\underline{BM}$, $y = 100 - x$, then the point d_1, i.e. the right end of the intercept d_0d_1 lies on the line $\underline{BM}$. In all such cases, where $\underline{x} > 100$, the right end of the intercept, indicating the composition of the component $\underline{x}$ in the material, will lie on the lower extension of $\underline{Db}$.

Let us assume that the value of $\underline{x}$ appearing in the equation with $\underline{y}$ is, in its turn, a function of two arguments, $\underline{x_1}$ and x_2, namely: $x = x_1 + x_2$.

In this way, we can go from two- to three-component compositions: $y + x_1 + x_2 = 100$.

In this case, it is necessary to locate one point (C on Fig. 1) on the intercept C_0C_1, where the intercept will be the sum of two intercepts C_0C and CC_1; x can be the sum of any number of components, and therefore the concept presented above is applicable to 4-5- and in general n-component materials. A definite number of points must be laid off on the horizontal intercept, representing the absolute value, according to the complications of the composition. The concentration triangle of the 3-component systems relates to the particular case where there is only one point on the line of composition C_0C_1.

For graphical calculation of raw Portland cement mixtures, there is a very important case where one of the components x is negative, while x itself remains positive.

Such a case of a 3-component mixture y', x'_1 and x'_2, is shown in Fig. 1, where for the sake of example we have taken $y = Oe_0 = -45$, $x'_1 = e_0e = 160$ and $x'_2 = ee_1 = -15$; the sum of all components will again be equal to 100, at the end of the intercept ee_1, i.e. the point e_1 lies on the line BM; the value x'_2 being negative, runs from right to left.

Let us now take the method of graphical calculation of any multi-component composition of a material with a smaller number of components. In Fig. 2 the line $C_0 - C_1 - C_2 - C_3$ represents the 4-component compositions: $y = OC_0$; $x_1 = C_0C_1$; $x_2 = C_1C_2$, and $x_3 = C_2C_3$ with $y + x_1 + x_2 + x_3 = 100$. We exclude the component x_3, i.e., we go over to the 3-component composition, $y' + x_1' + x_2' = 100$.

For this purpose, we draw the lines OC_1 and OC_2 from the origin. By excluding the component x_3, the absolute values of the remaining components should be increased in order to maintain the initial proportion between them. From what has been said above, it follows that when the line OC_2 cuts the hypotenuse Db in the point C'_2, the sum of the 3 remaining components will be equal to 100.

If we draw from the point C'_2 a horizontal line, we obtain the points C'_1 and C'_0; the intercepts OC'_0, $C'_0C'_1$ and $C'_1C'_2$ give the values of y', x'_1 and x'_2 sought for: $y' = OC'_0$, $X'_1 = C'_0 C'_1$ and $x'_2 = C'_1 C'_2$.

If we also exclude x_2, then we obtain 2-component compositions: $y'' + x_1'' = 100$ with $y'' = OC_0''$ and $x_1'' = C_0''C_1''$.

As will be seen from what follows, the calculation examined applies to clinker, raw material or lime materials, calculating them on a smaller number of components, in particular, calculating limestone as calcined substance.

Clay materials will occupy on the graph approximately the same position as the intercept d_0d_2 on Fig. 2. Calculation on the ignited substance of clay material, i.e. excluding the intercept d_1d_2, is shown in the lower part of Fig. 2.

A more general rule for such calculations may be formulated thus: for reducing the number of components it is necessary to draw a line through the origin and left end of the intercept, corresponding to the component excluded, adjacent to the line BM to intersection with this line, and through the point obtained to draw a horizontal line to intersection with the axis Oy; afterwards lines must be drawn through the origin and the right ends of the intercepts; the intercepts obtained on the new horizontal line determine the contents of the components in the composition being calculated.

If the component x which is excluded is negative, then the left end of the intersept lies to the right, (Fig. 1, point e, left end of the intercept e_1e)

Let us turn now to the examination of the diagrams made up for the calculation of cement charges.

Let us assume that in the clinker, composed of the oxides CaO, SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$, the sum of which comes to 100, the following compounds are formed: C$_3$A, C$_4$AF, and C$_m$S. Here, and also later on, the letter C is used for representing the compound CaO, the letter A for Al$_2$O$_3$, S for SiO$_2$ and F for Fe$_2$O$_3$. If m $>$ 2 then the formation of C$_2$S and C$_3$S should occur as a result of reaction between C$_m$S and the uncombined or excess lime, represented by C$_1$, remaining after the formation of C$_m$S, C$_4$AF and C$_3$A.

The quantity of excess lime C$_1$ can be calculated from the following formula:

$$C_1 = C - C_{C_m S} - C_{C_4 AF} - C_{C_3 A}, \tag{2}$$

where C is the total content of lime in the clinker, and C$_{C_3A}$, C$_{C_4AF}$ and C$_{C_mS}$ is the quantity of lime bound in the form C$_3$A, C$_4$AF and C$_m$S.
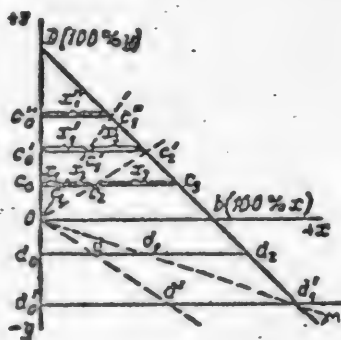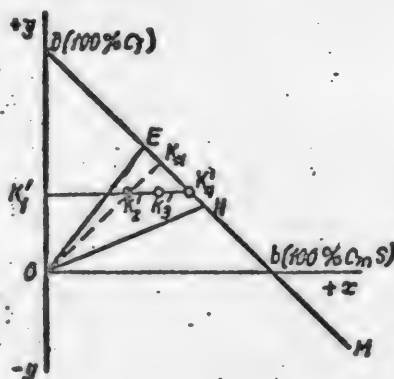
Fig. 2.   Fig. 3.

Let us lay off along the vertical axis Oy the value of the excess lime C$_1$, and along the horizontal axis Ox, all the other values. Consequently:
$\underline{x} = \underline{x}_1 + \underline{x}_2 + \underline{x}_3 = C_m S + C_4 AF + C_3 A$.

Thus, in Fig. 3 the point D will correspond to 100% C$_1$.

If C$_4$AF = 0, and C$_3$A = 0, then 100% $\underline{x}$ corresponds to 100% C$_m$S, i.e., the point $\underline{b}$.

If for a given clinker, C$_1$ is equal to the intercept DK$'_1$, then C$_m$S, C$_4$AF and C$_3$A can lie on the horizontal, drawn through the points K$'_1$ to intersection with the hypotenuse at the point K$'_4$. Then the intercepts K$'_1$K$'_2$, K$'_2$K$'_3$ and K$'_3$K$'_4$ will represent, on the scale taken, C$_m$S, C$_4$AF and C$_3$A:

K$'_1$K$'_2$ = C$_m$S, K$'_2$K$'_3$ = C$_4$AF and K$'_3$K$'_4$ = C$_3$A.

The collection of values C$_1$, C$_m$S, C$_4$AF and C$_3$A, we call the conventional mineral composition of the clinker.

When C$_4$AF = 0 and C$_3$A = 0, then only C$_1$ and C$_m$S figure in the provisional mineral composition of the clinker, i.e. C$_1$ + C$_m$S = 100, their different quantitative relationships, which follow a linear equation, will be graphically represented by a point lying on the line DM in Fig. 3.

Consequently, there should be in particular, on the hypotenuse, points

indicating the compositions C_2S and C_3S. On Fig. 3 it is taken that the point E corresponds to C_3S and point H to C_2S. According to Kind, C_3S corresponds to the coefficient of saturation KN = 1, and C_2S to the value KN = 0.667. Joining the point E to the origin, we obtain the line OE, for all points of which KN = 1, since the relation between C_1 and C_mS remains unchanged along it (see above).

In a similar way, all points on the lines ON have KN = 0.667. Above the point E lie compositions with KN >1, and all points on the line NM have KN< 0.667.

In correspondence with the order assumed for laying off values on the diagram (Fig. 3), C_1 and C_mS are represented by the co-ordinates of the point K'_2. Drawing a line OK'_2 to intersection with the hypotenuse in the point K_N, keeping the relation of C_1 to C_mS unchanged, we exclude the remaining components C_4AF and C_3A. The sum of C_1 and C_mS, in the two-component composition obtained, will be 100.

Representing the new values of C_1 and C_mS by C'_1 and C_mS', we write:

$$C'_1 + C_mS' = 100. \tag{3}$$

From what has been said above, it follows that the point K_N represents the coefficient of saturation of a definite value which is characteristic for the whole line OK_N. Thus, the line taken, passing through the origin and a point having the coordinates C_1, C_mS (e.g. point K'_2), gives a line of constant value of KN; we name it the KN line.

Let us deduce a general formula for the value of KN.

If we designate by C_S the line bound with silica in the form of different silicates, then the coefficient of saturation of the silica by the lime will be expressed as follows:

$$KN = \frac{C_S}{2,8S} \tag{4}$$

This formula, as follows from the above exposition, is to be used in cases where $C_S + S = 100$; hence,

$$S = 100 - C_S \tag{5}$$

The composition of the silicate lime C_S comprises lime existing in the form of silicate C_mS' (designated by C'_{C_mS}) and the excess lime C'_i, as a result of the reaction of which with C_mS, with m >2, C_3S and C_2S are obtained. Consequently, $C_S = C'_1 + C'_{C_mS}$.

The lime C'_{C_mS} may be represented also thus: $C'_{C_mS} = f_S \cdot S$ where f_S is a factor corresponding to the basicity of the silicate C_mS.

Inserting the values obtained into the expression for C_S, we have: $C_S = C'_1 + f_S \cdot S$.

Using (5), we find: $C_S = C'_1 + f_S (100 - C_S)$.

After rearrangement, we obtain: $C_S = \dfrac{C_1 + f_S \cdot 100}{f_S + 1}$

Introducing the value C_S into the Formula (4) and making the necessary rearrangement, we deduced the following expression:

$$KN = \frac{C'_1 + f_S \cdot 100}{2.8(100 - C'_1)} \tag{4a}$$

Formula 4a we present in a different form:

$$C'_1 = \frac{280 \, KN - 100 \cdot f_S}{1 + 2.8 \, KN} \tag{6}$$

There can be innumerable forms of Formula (6), since f_S can be given any value. Corresponding to this, different computational diagrams would be obtained. Evidently, the choice of formula should be conditioned by considerations of convenience and accuracy.

From Fig. 3 it is evident that on the given scale, the calculation of mixtures for given KN may be made more accurately, the larger the intercept EN, along which KN changes from 1 to 0.667. Instead of the intercept EN, the value C'_1 may be considered, determined from Formula (6) and depending on KN and f_S. With KN = 1 and KN = 0.667, we obtain respectively for C'_1:

$$C'_1 = \frac{280 - 100 \cdot f_S}{3.8} \; ; \qquad C'_1 = \frac{186.7 - 100 \cdot f_S}{2.87}$$

Thus, the difference between these values C'_1, which we represent by $\Delta C'_1$, proportional to the intercept EH, will be: $\Delta C'_1 = 8.58 \cdot (1 + f_S)$.

When $f_S = 0$, i.e. when instead of the silicate C_mS silica is present in the provisional mineral composition, then $\Delta C'_1 = 8.58$. Such a case corresponds to the diagram of Grun and Kunze.

If the conventional mineral composition is calculated, allowing for the presence of C_2S, for which $f_S = 1.87$, then $\Delta C'_1 = 24.47$. This latter value is approximately 3 times larger than $\Delta C'_1$ at $f_S = 0$, and consequently, the intercept EN will be 3 times longer. Correspondingly, the calculation on the diagram characterized by $f_S = 1.87$ will be more accurate than on a diagram characterized by $f_S = 0$.

By increasing f_S the intercept EN may be lengthened as desired; however, it is most convenient to obtain a diagram with $f_S = 1.87$. When using such a diagram the accuracy of calculation is quite satisfactory, and all operations involved in the graphical calculation are most simple and rapid. Hence, the author suggests that the optimum diagram is that in which the triangle OEN is constructed for the value of $f_S = 1.87$. As indicated above, Grun and Kunze use the value $f_S = 0$ for the construction of this triangle, which is the least satisfactory.

A general form of the proposed computational diagram is shown in Fig. 4. To the point of the composition C_3S, namely E in Fig. 4, corresponds the content $C'_1 = 24.47$ calculated from Formula 6.

The point N for composition C_2S lies on the horizontal axis Ox, In using such a diagram all the silica must be calculated as dicalciumsilicate, which will be represented by C_2S_0 and called the total dicalcium silicate. Corresponding to this, the lime C_{C_mS} in Formula (2) should be replaced by $C_{C_2S_0} = 1.87 \, S$. In the expression (2), it is also necessary to allow for the lime bound with SO_3 in the form of $CaSO_4$ $(0.7 \, SO_3)$. Taking into consideration, apart from this, that $C_{C_4AF} = 1.4 \, F$ and $C_{C_3A} = 1.65 \, (A - 0.64 \, F)$, Formula (2) can be re-written thus:

$$C_1 = C - 1.87 \, S - 1.65 \, (A - 0.64 \, F) - 1.4 \, F - 0.7 \, SO_3 \tag{7}$$

Apart from this, it must be borne in mind, that in clinker and in the raw materials there is also magnesia and there may be some other oxides. These

"other" oxides will be designated O.

To simplify the calculation, the percent composition of MgO, $CaSO_4$ and O will be summed and designated by the value R, i.e. $R = MgO + CaSO_4 + O$. We shall call the united components R.

Consequently, the components of the conventional mineral composition of the clinker will be the following: C_1, C_2S_O, R, C_4AF and C_3A. The sum of these should naturally be equal to 100: $C_1 + C_2S_O + R + C_4AF + C_3A = 100$. The conventional mineral composition of the ignited materials will be expressed by the same components which enter into the composition of the clinker. For the unignited raw materials, there is still another component - the loss on heating L. Consequently, for uncalcined materials we have $C_1 + C_2S_O + R + C_4AF + C_3A + L = 100$.
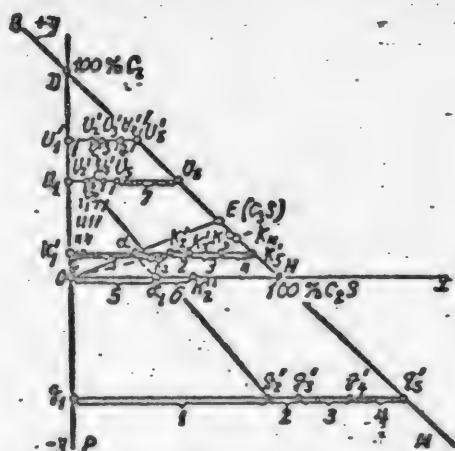
Fig. 4

1 - C_2S_O; 2 - R; 3 - C_4AF; 4 - C_3A;
5 - C_3S; 6 - C_2S; 7 - L. $x = C_2S_O +$
$+ R + C_4RF + C_3A + L$.

The conventional mineral composition is calculated for the oxide composition of the material: C_1 from Formula (7) and the remaining components from the following expressions:

$$C_2S_O = 2.87 \ S; \qquad (8)$$

$$R = MgO + CaSO_4 + O \qquad (9)$$

$$C_4AF = 3.04 \ F; \qquad (10)$$

$$C_3A = 2.65 \ (A - 0.64 \ F). (11)$$

Consequently, in the general case of completely conventional mineral composition, x is the sum of 5 components:

$$x = x_1 + x_2 + x_3 + x_4 + x_5 = C_2S_O + R + C_4AF + C_3A + L. \qquad (7)$$

which are laid off on the determined horizontal line of the computational diagram always in the indicated order. There can be 6 components of the provisional mineral composition, i.e. 5 components for x and 1 value for $y = C_1$. Certain of these can be negative, but the sum of all must be 100.

The horizontal line, determining the conventional mineral composition of the given material, we shall call the line or horizontal of the composition.

The linear value of the component in the material, which does not suffer loss on heating, we shall designate by letters with primes, and for uncalcined material, by letters without primes.

Let us assume that we have limestone and slag, the composition of which is presented in Table 1. In the composition of blast furnace slag, S, MnO, and FeO are previously calculated as SO_3 and Fe_2O_3 by the following formula: $SO_3 = 0.25 \ S$ and $Fe_2O_3 = 1.1 \ (FeO + MnO)$.

The conventional mineral composition of limestone and slag, calculated from Formulas (7-11), and likewise the linear values of the components, laid off on Fig. 4, are presented in Table 2.

The working diagram is constructed on the scale $1\% = 2.5$ mm.

Table 1
Table 1
Composition of Limestone and Blast Furnace Slag

Name of material	Ignition loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Others	Total
Limestone	42.96	0.62	0.46	0.07	54.87	0.65	0.20	0.14	100.00
Slag	--	38.44	15.34	3.58	38.85	3.55	0.16	--	100.12

Table 2
Conventional Mineral Composition of Limestone and Slag

Designation of Components of Conventional mineral composition	Limestone (in %)	Limestone Intercept on diagram	Slag (in %)	Slag Intercept on diagram
C_1	52.78	OU_1	-59.93	OG_1'
C_2S_0	1.78	U_1U_2	110.24	$G_1'G_2'$
R	1.13	U_2U_3	3.82	$G_2'G_3'$
C_4AF	0.21	U_3U_4	10.88	$G_3'G_4'$
C_3A	1.11	U_4U_5	35.08	$G_4'G_5'$
L	42.96	U_5U_6	-	-
Total	99.97		100.09	

As described above, the graphical calculation of limestone is made on the ignited substance. The Line $U_1'U_5'$ with the corresponding points on it, is the horizontal of the composition of the ignited limestone. On Fig. 4, the lengths of the intercepts do not in every case faithfully represent the corresponding magnitudes for reasons of clarity of representation. The C_3S content in the clinker is taken as 50%. The following relation, established by us [6], exists between C_3S and C_1: $C_1 = 0.2457 \, C_3S$. (12)

With the help of this formula, for the given quantity of C_3S in the clinker, we find $C_1 = 12.28$. On the axis Oy we lay off $OK_1' = 12.28$, and through the point K_1' we draw the line $K_1'K_5'$, which is simultaneously the line of composition of the clinker and the C_3S content in it. Actually, the intercept $\alpha K_5'$ being part of the line $K_1'K_5$, represents in the triangle OEN the line of constant C_3S content. Its quantity is determined by the intercept $O\alpha$ or the intercept $O\alpha_1$, proportional to it, which is obtained by drawing through the point α the line $\alpha\alpha_1$, parallel to the line EN.

Without carrying out a calculation of the proportion of materials in the raw mixture, we find the complete mineral composition of the clinker under consideration. To do this, we join by lines, one to another, points with identical indices on the horizontal compositions of the ignited limestone ($U_1'U_5'$) and slag ($G_1'G_5'$).

This construction is not shown on Fig. 4 and only the points $K_2'K_3'$ and K_4' on line of composition of the clinker are marked. On this latter, the point K_2' has the coordinates C_1 and C_2S_0. Drawing through K_2', a line $K_2'K_2''$ parallel to EN, we obtain on the ON the intercept OK_2''. The construction of the intercept OK_2'' described corresponds to joining C_1 to C_2S_0 according to the rule of nomography. Hence OK_2'' represents the sum $C_1 + C_2S_0$. Since $C_1+C_2S_0 = C_3S+C_2S$, then, as is evident from Fig. 4, $C_2S = \alpha_1K_2'' = \alpha K_2'$ The remaining components of the mineral composition of the clinker are obtained directly by measuring the corresponding intercepts (Fig. 4).

It must be remarked that the Formula (4a), deduced above for calculating KN, applies only to the compositions containing 2 components: C_1 and C_2S_0. For the calculation of the KN of clinkers with the usual number of components, other formulas must be deduced. In these clinkers the lime, present as silicate (C_S) may be considered as consisting of C_1 and lime, present in the form C_2S_0, the quantity of which is equal to $1.87S$: $C_S = C_1 + 1.87 S$.

Remembering that $S = \dfrac{C_2S_0}{2.87}$, Formula (4) may be rearranged to the following expression:

$$KN = 1.025\frac{C_1}{C_2S_0} + 0.667. \tag{4b}$$

From formulas, the deduction of which we omit, the mineral composition of the clinker may be used to calculate the silicate modulus ($\underline{n}$), the alumina modulus ($\underline{p}$) and the quantity of liquid phase ($\underline{L}$):

$$\underline{n} = \frac{C_2S_0}{1.09C_3A + 1.55C_4AF}; \tag{13}$$

$$\underline{p} = 1.15\frac{C_3A}{C_4AF} + 0.64; \tag{14}$$

$$\underline{L} = 1.12 \cdot C_3A + 1.35 \cdot C_4AF + R \tag{15}$$

For the determination of the proportions of materials in absolutely dry but unignited mixtures, we draw the line U_2G_2.

C_1 and C_2S_0 are the coordinates of the points, i.e. they determine the KN of the slag and uncalcined limestone. The point K_2' determines the KN of clinker. We draw a line through the point K_2' and the origin. Then, as was shown earlier, along the line OK_N we will have a constant value of KN, corresponding to the KN of the clinker considered, but since KN in the clinker and in the raw mixture are identical, then the point of intersection of the line U_2G_2 with the line KN (CK_2) determines the KN of the raw mixture and simultaneously the proportions of the raw mixture.

This proportion is determined by the usual rules as follows:

Fraction of limestone in the mixture $\underline{x}_U = \dfrac{K_2G_2'}{U_2G_2'}$;

Fraction of slag in the mixture $\underline{x}_G = \dfrac{K_2U_2}{U_2G_2'}$.

For the case under examination was found: $\underline{x}_U = 0.611$ and $\underline{x}_G = 0.389$.

For this proportion, the composition of the raw mixture was calculated and afterwards the mineral composition of the clinker and all its characteristics. These values are compared (Table 3 "analytical" line) with the composition obtained from the graph and by additional calculation from the Formulas indicated above (Table 3, "graphical").

From Table 3 it is seen that the divergence between the value of C_3S assumed for the calculation (50%) and that obtained by analytical calculation from the composition of the mixture (49.3%), is 0.7. Such a deviation is admissible not only for plant production of Portland cement, but also for laboratory investigations. It must be noted that the example presented relates to a number of the least accurate calculations. Usually, the deviations from the given value of C_3S vary within the limit of 0.3-0.5 abs. %. The same is true for C_2S. The deviation for C_3A and C_4AF is lower than for C_3S. Corresponding to small deviations for C_3A and C_4AF, the values for the liquid phase also differ little. Differences

in values of the moduli are usually observed in the second decimal place (Table 3); KN "graphical" differs from "analytical" in the third decimal place.

Table 3
Comparison of Values Obtained Graphically, With Values Calculated Analytically, For the Proportions of Materials in Mixtures

Method	C$_3$S	C$_2$S	R	C$_4$AF	C$_3$A	KN	L	p	L
Graphical	50 (given)	22.0	2.9	5.9	19.6	0.878	1.95	4.46	30.70
Analytical	49.30	22.35	2.96	5.92	19.42	0.874	1.98	4.36	30.70
Difference	0.7	0.4	0.1	0	0.2	0.004	0.03	0.10	0

SUMMARY

Methods worked out by the author using rectangular coordinate systems may be used not only in the cement industry but also for those cases where it is required to calculate raw mixtures from some materials, for example, for the calculation of glass charges.

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EFFECT OF ACIDITY OF SOLUTION AND OF IMPURITIES

ON THE CRYSTALLIZATION OF AMMONIUM SULFATE

M.A. Rabkin, A.P. Romanenko and M.E. Kovalskaya

Laboratory of General Chemistry, Zhdanov Metallurgical Institute

Ammonium sulfate is obtained in the main by the following two methods: 1) interaction of sulfuric acid with ammonia; and 2) by passing coke oven gas containing ammonia through a solution of sulfuric acid. The latter method is the more economical and is used in the majority of new plants.

For application, it is desirable that the ammonium sulfate is obtained in the form of a free flowing mass and that on storage it does not become converted to a compact mass, requiring extra energy for grinding. It has been observed that coarsely crystalline ammonium sulfate shows a smaller tendency to cake, compared with finely crystalline. It therefore appeared of interest to study how different factors affect the size of the crystals of ammonium sulfate. Coke oven gas, depending on its degree of purification, may contain various impurities, of which the main ones are pyridine bases and tarry substances. It may be assumed that the impurities contained in the coke oven gas have an effect on the size of the crystals of ammonium sulfate. A more important factor is the concentration of sulfuric acid through which the coke oven gas is bubbled.

The study of the effect of the factors indicated on the size of the crystals of ammonium sulfate obtained, is contained in the investigational data.

Method of investigation. For carrying out the experiments, technical, thrice recrystallized ammonium sulfate was used, from which a solution saturated at 60° was prepared. At this same temperature, we took from the general solution a volume, such that, on addition of sulfuric acid, the quantity of which was varied in different experiments, 50 ml of solution was obtained. Before this, we determined the ammonium sulfate content in 1 ml of saturated solution, and found it to be 0.576 g/ml. In the solutions of ammonium sulfate and sulfuric acid, we dissolved 0.576 g of $(NH_4)_2SO_4$ in addition, in each ml of sulfuric acid.

The solutions, which in the process of carrying out the experiment, cooled somewhat, were heated to 70°, after which they were slowly cooled. The temperature was noted at which crystals first began to separate, and afterwards, when the temperature had fallen to 20-25°, and the mother liquor had been decanted, the size of the crystals was measured.

Effect of concentration of sulfuric acid on size of crystals. The results of the study of the effect of concentration of sulfuric acid on the size of the crystals of ammonium sulfate separated are presented in Table 1.

As can be seen from Table 1, the size of the crystals increases with the acidity from the start, attains a maximum size at 9-15 g/liter of acid, and with further increase of the concentration of acid, the size diminishes. This is also illustrated by photographs of crystals obtained at concentrations of sulfuric acid of 0.5, 1.5, 9.0, 12.0, 18.0, 27.0 and 36.0 g/liter.

In parallel with the change of the size of ammonium sulfate crystals, a change of the temperature at which the first crystals formed was observed. From

Table 1
Effect of Sulfuric Acid Concentration on the Crystallization of Ammonium Sulfate

H_2SO_4 content (in g/liter)	Temp. of initial crystallization (in °C)	Size of crystals (in mm) length	breadth	Remarks
0.5	45	2-3	2-1	
1.0	45	5-8	1-3	
1.5	55	8-10	3-4	
3.0	58	10-12	3-5	
6.0	64	10-12	3-5	
9.0	55	12-23	3-5	
12.0	48	25-43	4-5	
15.0	32	30-35	3-5	
18.0	30	20-30	2-5	
21.0	30	20-30	2-5	
24.0	30	18-25	2-3	

H_2SO_4 content (in g/liter)	Temperature of initial crystallization (in °C)	Size of crystals (in mm) length	breadth	Remarks
27.0	28	10-15	1-2	
30.0	28	8-10	1-2	
33.0	24	5-7	0.5-1	
36.0	18-20	4-5	0.5-1	
39.0	18-20	4-5	0.5-1	
42.0	18-20	4-5	0.5-1	On long standing
45.0	Did not crystallize	--	---	
48.0	--	--	---	
51.0	-	--	---	

a comparison of the temperatures of initial crystallization, it can be concluded that ammonium sulfate with a small content of free sulfuric acid tends to form supersaturated solutions. Crystallization from supersaturated solutions yielded fine crystals. With increasing acidity, the tendency to formation of supersaturated solutions falls, and at the same time an increase in the size of the ammonium sulfate crystals was observed.

The lowering of the temperature of initial crystallization at concentrations of sulfuric acid higher than 6 g/liter can be explained by the fact that, under these conditions, an acid salt is partially formed, which has a higher solubility [1].

The coarsest crystals were obtained at concentrations of sulfuric acid which corresponded to a somewhat elevated solubility of ammonium sulfate. In these conditions, a comparatively small number of crystallization centers are created, which favors the formation of large crystals.

Effect of impurities on crystallization of ammonium sulfate. We carried out a series of experiments of once recrystallized ammonium sulfate, in which a considerable part of the impurities of the technical product was retained. Apart from the presence of impurities, all the conditions of carrying out the experiment remained the same.

The relations between the size of crystals and the acidity of the solution, established for ammonium sulfate containing no impurities, were reproduced in the given series of experiments with the product containing the normal impurities in technical ammonium sulfate. However, the absolute size of the crystals in each of these experiments was smaller. The maximum size of the crystals in experiments with ammonium containing impurities was 10-12 mm.

In order to determine how the impurities induce a decrease in the size of crystals, we carried out experiments with pure ammonium sulfate to which different quantities of pyridine and tars were added, these being obtained as secondary
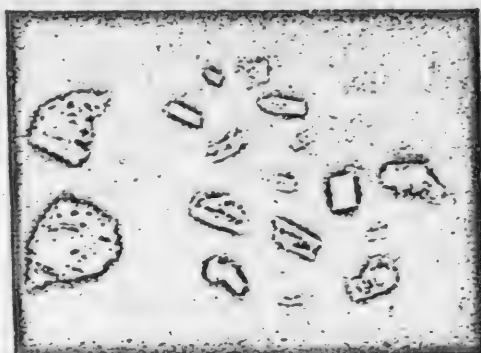
Crystals of ammonium sulfate at
different concentrations of H_2SO_4.

Concentration of H_2SO_4
in g/liter:

a) 0.5;   b) 1.5;   c) 9;   d) 12;

e) 18;   f) 27;   g) 36.
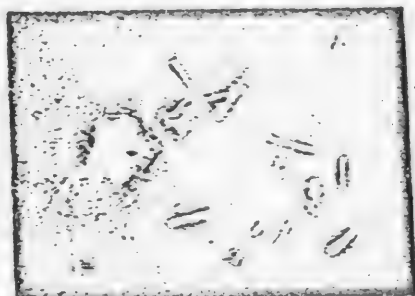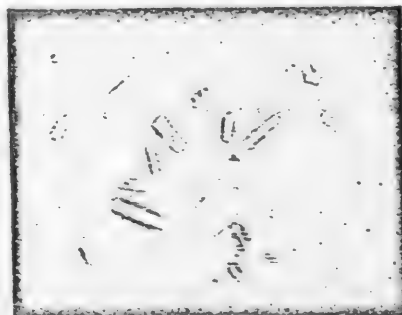
products of coking. It was established that pyridine and tar only change the color of ammonium sulfate, but do not affect its crystal size. The experiments moreover showed that the decrease in the size of the crystals is caused by the water-soluble impurities which give a yellow color to the mother liquor; we did not determine their chemical composition. The crystallization proceeds in a completely different manner in the presence of water soluble impurities: a solid, brittle film was formed on the surface which after some period of time fell to the floor of the beaker, after which a new film began to form in the upper part of the solution.

It is possible that in this case, the reduction in size of the crystals and the specific character of the crystallization is bound up with the presence of water-soluble low-molecular coking products. Their action may be explained by their surface activity. As was shown by Rebinder, in the presence of surface active substances, the size of crystals formed during crystallization diminishes [2].

Effect of additions on crystallization of ammonium sulfate. We investigated the action of the following substances: Phosphoric acid and ammonium phosphate, ammonium chloride, nitric acid and ammonium nitrate. Experiments showed that phosphoric acid, ammonium phosphate and nitric acid in small quantities (0.3 to 3 g/liter) had no perceptible effect on the crystallization of ammonium sulfate. After addition of 3 g/liter ammonium chloride, crystals appeared only after long standing (24-72 hours).

Table 2

Effect of Additions of Ammonium Nitrate on the Crystallization of Ammonium Sulfate

Solution of ammonium sulfate saturated at 60°. Free H_2SO_4 1.5 g/liter.

NH_4NO_3 concentration (in g/liter)	Characteristics of ammonium sulfate crystals	Remarks
0.0	8-10 mm	--
3.0	Fine needles	Crystallization started after 3 days
6.0	Fine plates	--
9.0	Plates up to 10 mm	--
12.0	Plates up to 10-15 mm	--
15.0	Plates up to 10-12 mm	--
18.0	Small acicular crystals	Crystallization started after some days at room temperature
21.0	Ditto	--

It was particularly interesting to study the effects of additions of ammonium nitrate, since nitric acid may be present in technical sulfuric acid, and by passing coke oven gas through the solution, a certain quantity of ammonium nitrate may be formed along with ammonium sulfate. We studied the effect of ammonium nitrate added to saturated solution of ammonium sulfate, containing 1.5 g/liter sulfuric acid. The concentrations of ammonium nitrate in the individual experiment were 3.0, 6.0, 9.0, 12.0, 15.0, 18.0 and 21.0 g/liter (Table 2).

As can be seen from the data in Table 2, saturated solutions of ammonium sulfate are obtained in the presence of ammonium nitrate at certain concentrations (3-6 and 18-21 g/liter).

In the crystallization of ammonium sulfate from supersaturated solutions, fine plate-shaped or acicular crystals are obtained.

SUMMARY

1. To obtain large crystals of ammonium sulfate from solutions containing free sulfuric acid, the optimum concentration of the latter should be brought to 9-15 g/liter.

2. The impurities introduced into the solution from unpurified coke oven gas lower the size of ammonium sulfate crystals but the following regularities are maintained in the presence of these impurities: the size of the crystals increases as the concentration of sulfuric acid increases up to 9-15 g/liter, but further increase of concentration of acid leads to a lowering of the crystal size.

3. By investigating the effect of different additions to solutions of ammonium sulfate, it was found that certain concentrations of ammonium chloride and nitrate impede the process of crystallization. Crystallization begins after long standing at room temperature and fine plate-like or acicular crystals of ammonium sulfate are formed.

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STABILITY OF ANODES OF LEAD AND ITS ALLOYS
IN THE ELECTROLYSIS OF SULFATE SOLUTIONS

G.Z. Kiryakov and V.V. Stender

In the electrolysis of sulfate solutions, "insoluble" anodes of lead and its alloy with 1% of silver find application. As the electrolysis proceeds, these anodes corrode, and the products of their decomposition contaminate the cathode metal; the high anode potential is a large and unproductive component in the p.d. across the cell [1].

The processes which occur at lead anodes in sulfate solutions are similar to those which occur on the positive plates of the lead-acid accumulator during its discharge [1,2,3] with only this difference, that for raising the capacity and the strength of the discharge current of the accumulator, all the conditions for facilitating the transfer of lead and its compounds into solution are created while in the operation of a lead anode, every effort must be directed to repress the transfer of lead into solution. In the accumulator, the highest possible positive potential of the electrode is aimed at, and in electrolysis the lowest possible.

Numerous investigations aimed at raising the stability and lowering the potential of lead anodes have led to attempts to introduce certain salts into the electrolytes and mainly to introduce various alloy additions into lead.

Cobalt ions in small quantity appear to be particularly effective additions to the electrolytes. According to data of Krivolapova and Kabanov [4], 0.1% cobalt sulfate on the weight of electrolyte, 6-7 N in acid, raises the stability of lead anodes at small current densities and lowers the potential by 0.05 V; Rey and co-workers [5], discovered that when the cobalt content in solution increases, the stability of the anode increases. These authors tried to explain the action of cobalt ions as being due to their facilitating the discharge of sulfate ions, and to the difficulty of forming lead persulfate in their presence, and also to the fact that cobalt facilitates the formation of compact protective films on the anode. It is known that the presence of cobalt ions in a zinc electrolyte causes a lowering of the current efficiency for zinc (6), and hence they are not desirable from the point of view of cathode processes.

Apart from silver, many metals in binary, ternary and quaternary alloys have been tried as alloy additions to lead. Mashovets and Lyandres [7], studied the anodic stability of lead alloys with antimony, arsenic, bismuth, iron, zinc, magnesium and calcium under the conditions of operation of the lead accumulator and established that, apart from a small quantity of arsenic and calcium, the other alloy additions lowered the stability of the anodes. Konig and co-workers [8], in trying out anodes of binary alloys of lead with bismuth, arsenic, antimony, tin, silver and magnesium, under conditions of electrolysis of zinc, interested themselves mainly in the anode potential and purity of the cathodic zinc. These authors established that the quality of the zinc was best with lead-silver anodes; cadmium and tin gave cathodic deposits with a lustrous surface; arsenic, antimony and bismuth induced a decomposition of the cathodic zinc; with silver alloys, a lowering of the potential of the anode by 0.12 V was found, by comparison with pure lead. Tainton and co-workers [9] also studied numerous alloys

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[1] Communication I of a series in this field.

and found that the best results for stability were given by binary alloys of lead with 1% silver and ternary lead-silver-arsenic or -tin alloys. Fink and Eldridge [10] found that alloys of lead with 2-4% of thallium were particularly stable in the presence of nitrate and chloride ions as impurities in the electrolytes. Bray and Morral [11] indicated the stability of quaternary alloys of lead with 3.5-5.0% Tl, 0.003-0.03% Te, and 0.05-1.0% Ca.

From an examination of the results of all this work, it can be deduced firstly, that at present no alloys have been found superior to lead with 1% silver and secondly, that all the investigators selected their alloy metals more or less empirically, and were not guided by any basic concept in the choice of this or that addition.

The mechanism of the protective action of silver and other alloy additions to lead has so far not been satisfactorily explained. Evans [12], Tainton [9], Fink [10], and certain other authors explained it by the formation of compact protective films on the anode; Hire and Stears [13] noted a useful effect of tellurium in increasing the fine-grained structure of lead [14], Werner [15] considered that an increase in the graininess of lead is deleterious. König and co-workers [8] consider that additions of silver and certain other alloying metals to lead are useful because, by their solution, the surface of the anode increases, the anode current density falls and this results in a lowering of the rate of corrosion; the latter assumption is quite absurd. Heckler and Hanemann consider that one of the causes of the increase of stability of certain alloys of lead to corrosion in hot sulfuric acid without anodic polarization is the formation of micro-elements on the surface of the alloy; however, these authors do not distinguish between the action of substances like copper, nickel, platinum, bismuth and graphite, which are so different in their electro-chemical properties.

The empirical selection of alloying additions and the absence of a general theoretical approach to the question appears to be the reason why "insoluble" anodes of lead and its alloys do not last more than $1\frac{1}{2}$-2 years and do not permit cathode metal (zinc in particular) of high purity to be obtained.

In our work, a first attempt has been made to create a general concept about the mechanism of decomposition and protection of lead when using it as a cathode in the electrolysis of sulfate solutions. This paper reports the first part of the investigation, subdivided as follows: 1) anode stability of lead and of its alloys by change of weight; 2) potential of lead anodes and of their alloys; and 3) binary electrochemical systems composed of lead and alloying additions.[1]

Anode Stability of Lead and of its Alloys by Change of Weight

The selection of alloying additions was made in our investigation on the basis of the following concepts: 1) It is known from the literature and from practice that the most stable anodes are those of lead with 1% of silver; the fusion diagram for the system lead-silver has the usual appearance of a diagram for a binary alloy, showing no solid solutions, and has a eutectic at 2.5% Ag [16]. 2) We supposed that a more uniform distribution of silver in the alloy and a greater effectiveness of its protective action would be obtained if a third component were introduced into the system, forming solid solutions both with lead and with silver; as such additions, we tried Tl, Bi, Hg and Sn. 3) Gold, platinum and mercury in binary alloys were of interest to us as electropositive metals from which, in principle, the same protective actions could be expected, as from silver. 4) We paid attention to cobalt because of the high stability which

[1] Generalized results of this investigation as a whole will be given at the end of the third paper.

has been shown for lead anodes in the presence of dissolved Co^{++} ions [4,5], but cobalt does not give alloys with lead [16], and alloys containing it can only be produced by using a 3rd component according to the principle expounded above. 5) Information in the literature about the beneficial effects of As and Te in complex alloys is worthy of attention; in view of the small availability of Te, we tried its analog, Se, as well. and 6) Alkaline earth metals: Ca, Ba and Sr were of interest, first because they give with sulfuric acid salts of low solubility and should co-operate with it in the formation of protective films on the anode; secondly, in the literature there are many contradictory reports about the beneficial action of calcium on the stability of lead.

EXPERIMENTAL

Preparation of the alloys. The basic initial material was lead of a definite grade. The alloying additions were introduced into the lead in the form of more concentrated alloys, the composition of which was checked by chemical analysis. The silver alloy was introduced into lead below a layer of carbon in a crucible furnace; the alloys of other metals were introduced into the melt outside the furnace. After the introduction of the stock alloy, the mixture was carefully stirred. Silver and mercury for alloying were subjected to previous chemical purification; Te and As were chemically pure; the Sb was electrolytic; Co, Au and Sn were the highest commercial grades; Tl was pure, a product of another investigation; Se and Bi were technical products; Ba, Sr and Ca were introduced into the lead by electrolysis of the corresponding pure molten chlorides. It may be remarked that we did not find any literature reference to the electrolysis of the molten strontium chloride with a liquid lead cathode, and apparently this is the first time this has been done.

We examined all the alloys we prepared under a microscope with a magnification of 80-600; slices were prepared according to the proposals of Abulakh, whereby the alloy was poured onto a smooth glass plate heated to 85-90°. Microphotographs showed, for example, that binary alloy of lead with thallium had a homogeneous structure of solid solution; in the alloy of lead with 1% silver, the presence of fir-shaped inclusions of eutectics with 2.5% silver was quite clearly evident; in the ternary alloy of lead − 1% silver − 1% thallium the evidence of a eutectic became clear only at large magnifications and very fine fir-shaped inclusions were distributed considerably more uniformly. . The latter confirmed our original idea about an increase of uniformity of distribution of silver in an alloy by introducing a third component.

From the alloys, anodes were cast for investigating their stability in electrolysis. The steel mold had the form of a comb: before pouring it was coated internally with a fine layer of chalk. During casting, the mold was stood upright. The lead comb obtained, after casting, was cut up into separate electrodes, having the form of an extended inverted U [7]. Several electrodes were prepared simultaneously, identical in composition and in casting conditions. The choice of electrode form was determined by the need for measuring its electrical conductivity before and after use as an anode [7].

The method of determining the anode stability of lead and its alloys differed little from that used by Mashovets [7]. The anodes of the alloy under investigation, with copper contacts clamped to both their ends, were weighed and set up in a glass rectangular vessel with a working capacity of 50 ml, between 2 cathodes of pure lead, identical in form with the anode. The electrolyte was pure 2 N sulfuric acid. In special experiments, 100-500 mg/liter of chloride ions were introduced into the electrolyte. The anode current density in the majority of experiments was 400 A/m^2. Individual experiments were carried out at other current

densities up to 10,000 A/m^2 and other acidities – 4 N and 6 N. The working surface of the anode was 15 cm^2, and its average weight was 23 g. Two samples of each alloy were examined simultaneously. The electrolytic cells were joined in series in 7-8 units.

The electrolysis was carried on continuously day and night without external heating at around 25°. The losses of electrolyte were made up twice a day. After each 100 ampere hours the current was interrupted (at 600 mA this was after 167 hours, or 7 days continuous running) and the anodes were extracted, washed, air dried for a day and then weighed to an accuracy of 5 mg. The deposit of lead peroxide which had fallen to the floor of the cell was washed, dried and weighed separately. Where necessary the products of corrosion on the anode were removed, i.e. the film of lead peroxide which formed on them, containing the products of decomposition of the alloying components. To remove the film the anodes were immersed for 2 days in a mixture of equal volumes of a saturated solution of sodium acetate and 1 N thiosulfate [7]. For the majority of anodes the electrolysis was carried on for periods of the order of 300 and more ampere hours, i.e. for 3 weeks or more. Some samples were tested under continuous polarization for 4 weeks, (668 hours. i.e. 400 amp. hrs.).

In all cases of electrolysis the comparison anode was lead alloyed with 1% of silver. At the beginning of the test, and after each weighing, the electrical conductivity of the sample was determined to an accuracy of ±0.00005 Ω, it emerged, however, that the variations of electrical conductivity in the majority of alloys was small [7-10% on the initial value during 500 hours (300 amp.hrs.)], and was of no significance.

The results of the investigation of the stability of anodes of lead and its alloys are shown in Tables 1-5 in the form of the averaged data of two or more samples.

The loss of weight of the anodes and the weight of the slime was calculated as g/m^2. In the graph alongside, the differences in weight of the anodes after electrolysis from their weight before electrolysis are shown, the former weights always include the protective films not removed from the anode. For lead-silver alloys and lead-thallium alloys the weight of these films was in all cases practically identical. For anodes containing additions, with compact protective films (Ca, Ba, Sr, Sn, As) the weight of these films was determined separately.

From the data of Table 1 it can be seen that the alloy of lead with 1% of silver is considerably more stable than pure lead or its alloy with 0.5% of silver. The alloy of lead with 2% of thallium was of approximately the same stability as an alloy with 1% of silver, 9% of Tl in a binary alloy increased the stability of lead still more. But in spite of everything it must be admitted that the protective action of Tl alone is less than that of silver alone. In the ternary alloy Pb-Tl-Ag the effect of even small additions of Tl was very considerable; this is evidently due to the more uniform distribution of the silver and the presence of a third component, and it confirms one of our initial ideas about the selection of

Loss in weight of anodes of lead and its alloys during electrolysis in 2 N H$_2$SO$_4$ containing 100 mg/liter of Cl$^-$, at a current density of 400 Amp./m^2.
A – loss of weight(in g/m^2);
B – time (in hours).
1 – Pb – 99%,Ag – 1%; 2 – Pb – 98%, Ag – 1%, Se – 1%; 3 – Pb – 97%. Ag – 1%, Tl – 2%; 4 – Pb – 98%, Ag – 1%, Ca – 1%; 5 – Pb – 98.68%, Ag – 1%, Sn – 0.3%,Co – 0.02%.

alloying components (see above). The ternary alloys with 0.5% of Ag and 2.0 and 9.0% of Tl are very stable. The action of Te is practically imperceptible; considerable additions of Se perceptibly increase the stability of lead-silver alloys. Bi scarcely affects the stability; Ca in small quantities increases it, though the effect diminishes with time: the same is true for selenium. Au and Hg considerably lower the stability even during the first period of test.

Industrial sulfuric acid electrolytes frequently contain Cl⁻ as an impurity. It is usually considered [1] that this lowers the stability of lead electrodes. But even in 1935 one of us showed [17] that in the electrolysis of solutions of sodium sulfate containing 500 mg/liter of Cl^-, anodes of Pb with 1% of Ag have a considerable stability. The formation of AgCl produces a compact protective film on the anode.

Table 1

Loss of Weight of Anodes of Lead and its Alloys in the Electrolysis of Sulfuric Acid at a Current Density of 400 Amp./m²

No. of Alloy	Composition of anode alloy (in %)									Loss of weight (in g/m²) after the following times (hours)			Weight of slime (in g/m²) after the following times (hours)		
	Pb	Ag	Tl	Te	Se	Bi	Ca	Au	Hg	167	334	500	167	334	500
1	100.0	-	-	-	-	-	-	-	-	850	2040	3250	740	1620	3060
2	99.0	1.0	-	-	-	-	-	-	-	169	416	760	150	420	740
11	99.5	0.5	-	-	-	-	-	-	-	260	540	880	230	620	860
12	98.0	-	2.0	-	-	-	-	-	-	197	500	804	300	640	1020
13	91.0	-	9.0	-	-	-	-	-	-	60	220	410	134	338	540
14	99.3	0.5	0.2	-	-	-	-	-	-	175	410	620	120	420	1260
15	99.0	0.5	0.5	-	-	-	-	-	-	110	388	760	106	400	980
16	98.5	0.5	1.0	-	-	-	-	-	-	20	29	80	20	87	-
17	98.0	0.5	1.5	-	-	-	-	-	-	13	26	90	57	67	-
18	97.5	0.5	2.0	-	-	-	-	-	-	10	20	45	44	52	150
10	90.5	0.5	9.0	-	-	-	-	-	-	11	18	30	50	47	135
19	99.3	0.5	-	0.2	-	-	-	-	-	230	550	820	153	420	860
20	99.5	0.5	-	0.5	-	-	-	-	-	188	540	820	186	460	850
23	97.5	0.5	-	-	2.0	-	-	-	-	76	143	170	72	161	-
22	97.5	0.5	-	-	-	2.0	-	-	-	239	420	810	169	360	-
21	99.0	0.5	-	-	-	-	0.5	-	-	+4	123	330	-	-	-
24	99.0	-	-	-	-	-	-	1.0	-	596	-	-	-	-	-
25	98.0	1.0	-	-	-	-	-	-	1.0	620	-	-	-	-	-

In Table 2 the results of some experiments are shown, from which the effect of different quantities of chloride ions on the anode stability of some alloys can be deduced. (As the Cl ions were used up, they were replaced by additions of HCl).

From the data of Table 2 we see that addition of 500 mg/liter of Cl⁻ to the electrolyte in all cases increased the corrosion of the anode, mainly by attack at the electrolyte-air interface. In the presence of 100 mg/liter Cl⁻, the corrosion of the control specimens of lead alloyed with 1% of Ag was practically unchanged by comparison with pure electrolyte, in spite of the fact that pure lead corrodes strongly in solutions containing chloride ions; this affirms the protective action of the film of AgCl. By comparing the corrosion of samples of Alloy No. 2 with that of Alloys Nos. 28-29, it can be seen that the introduction of Tl stabilizes anodes in solutions containing 100 mg/liter Cl⁻ considerably.

Table 2

Loss of Weight of Anodes of Lead and its Alloys During the first 167 Hours of Electrolysis at 400 amp./m^2 in 2 N H_2SO_4 containing 0, 100 and 500 mg/liter of Cl$^-$

No. of Alloys	Composition of anode alloy (in %)					Loss of weight (g/m^2)	Weight of slime (g/m^2)	Loss of weight (g/m^2)	Weight of slime (g/m^2)	Loss of weight (g/m^2)	Weight of slime (g/m^2)
						Cl$^-$ (mg/l)					
						0		100		500	
	Pb	Ag	Tl	Se	As						
1	100.0	−	−	−	−	850	740	3300	−	−	−
2	99.0	1.0	−	−	−	169	150	120	197	472	700
14	99.3	0.5	0.2	−	−	175	120	−	−	73	679
17	98.0	0.5	1.5	−	−	13	57	−	−	489	558
28	98.9	1.0	0.1	−	−	140	195	+9	160	−	−
29	97.0	1.0	2.0	−	−	5	35	+5	60	−	−
23	97.5	0.5	−	2	−	76	72	−	−	719	1027
21	99.0	0.5	−	−	0.5	+4	−	−	−	650	976

In Tables 3 and 4 are set forth the results of testing the anode stability of a number of alloys in 2 N H_2SO_4, containing 1000 mg/liter of Cl$^-$.

Table 3

Loss of Weight of Anodes of Lead and its Alloys in the Electrolysis of 2 N H_2SO_4 Containing 100 mg/liter Cl$^-$, at a C.D. of 400 amp./m^2

No. of Alloy	Composition of anode alloy (in %)					Loss of weight (g/m^2) after (hours):			Weight of slime (g/m^2) after (hours):		
	Pb	Ag	Tl	Ca	Se	167	334	500	167	334	500
2	99.0	1.0	−	−	−	120	350	610	197	290	490
28	98.8	1.0	0.1	−	−	+9	170	280	160	260	340
29	97.0	1.0	2.0	−	−	+5	130	190	60	120	197
30	98.9	1.0	−	0.1	−	105	320	550	108	270	305
31	98.9	1.0	−	1.0	−	+67	10	86	40	100	205
32	98.9	1.0	−	−	0.1	19	155	280	50	155	250
33	98.0	1.0	−	−	1.0	70	309	250	95	270	430

The data of Table 3, in the first place, confirm the considerable stability of ternary alloys of Pb-Ag-Tl; secondly they show that the stability of alloys containing Ca and Se, which is initially high, begins later to fall rapidly at a rate proportional to a power of the time higher than unity (see Fig.); the explanation of this may be that as the third component dissolves from the surface layer its alloying effect naturally weakens.

Tainton [9] and Mashovets [7] noted the beneficial effect of As in Pb alloys on the stability of anodes. We tested alloys of lead with silver, containing As and Sb, during prolonged electrolysis. The results showed that a Pb-Ag-As alloy is less stable than the same alloy without the As addition; increase in the As content leads to a decrease of the anode stability; the same thing happens with Sb. A considerable increase of the weight of the protective film on them is characteristic of those anodes which contain As and Sb.

The thick and compact films formed on lead anodes hinder the diffusion of ions of Pb^{2+} into the electrolyte and so facilitate the oxidation of these ions to the tetravalent state, in which they are then hydrolyzed to lead peroxide. During prolonged electrolysis in 2 N sulfuric acid with pure lead anodes, the cathode

becomes covered with a thick sponge of metallic lead, formed as a result of the discharge of Pb^{2+} at the cathode; in 100 amp. hrs., according to our observations, 270 mg of spongy metallic lead is formed on the cathode. If anodes containing alloying additions which facilitate the formation of thick and compact protective films on them are used the quantity of lead deposited on the cathode falls to a few milligrams. To diminish the quantity of lead in the cathode metal (e.g., zinc) it is necessary to impede the transfer of Pb^{2+} ions into solution, in such a way that the rate of deposition of lead from solution at the cathode exceeds the rate at which it is fed into the solution at the anode.

Table 4

Loss of Weight of Anodes of Alloys of Lead with Silver, Barium and Strontium in the Electrolysis of 2 N H_2SO_4, containing 100 mg/liter of Cl^- at 400 amp/m^2

No. of Alloy	Composition of anode alloy (in %)				Loss of weight (g/m^2) after (hours):						Weight of slime (g/m^2) after (hours)
	Pb	Ag	Ba	Sr	167	334	500	678	845	1012	
2	99.0	1.0	–	–	104	200	360	475	580	740	670
41	95.0	–	5.0	–	725	1440	4240	–	–	–	2670
42	99.0	–	1.0	–	387	–	–	–	–	–	590
43	94.5	0.5	5.0	–	72	100	150	290	420	1050	1540
44	98.0	1.0	1.0	–	29	60	190	420	–	–	980
45	98.75	0.25	1.0	–	190	550	–	–	–	–	760
46	99.0	0.5	0.5	–	270	435	530	760	–	–	1940
47	99.0	–	–	1.0	555	–	–	–	–	–	460
48	96.5	0.5	–	3.0	7	70	–	–	–	–	160
49	98.5	0.5	–	1.0	30	300	–	–	–	–	420
50	98.0	1.0	–	1.0	10	70	–	–	–	–	170

Tests of the electrolysis of zinc under industrial conditions with anodes of the fairly stable ternary alloy No. 34 (Pb 34.17, Ag 0.43, Tl 0.80 and No. 35 (Pb 98.57, Ag 0.43, Ca 1.00) in sequence with anodes of the usual Pb-Ag alloy for 2 months continuous working, showed that the Pb content in the cathodic Zn in all three cases was identical and varied between 0.005 and 0.007%. Thus, large corrosion resistance of anodes is not a necessary condition for the cathode metal to contain a smaller quantity of lead.

To thicken the protective films and to render them more compact we introduced, into the anode alloys, metals giving salts of low solubility with sulfuric acid: Ba, Sr (forming sulfates) and Sn (forming products of the hydrolysis of the sulfate). In Table 4 are set out the results of the normal testing of alloys of lead and silver with barium and strontium; in Table 6, data relative to the same alloys, and alloys with As and Sn with indications of the weight of protective film on the anode are given. In the same table will be found the results of testing quaternary Pb-Ag-Sn-Co alloys.

In stability the binary alloys of lead with barium and strontium are clearly inferior to the comparison alloy No. 2; the ternary alloys of these metals with lead and silver are somewhat superior in weight loss at the beginning of test, but the large weight of slime which they produce shows that they suffer considerable decomposition and that there is a rapid precipitation of protective films on them.

The question of the positive effect of dissolved cobalt on the stability of lead anodes, raised by a number of authors [4, 5], was of interest and at the same time difficult to resolve in practice, because cobalt ions are detrimental to cathode processes [6]. This induced us to try to get metallic cobalt into the anode itself. We supposed that the cobalt in the anode would dissolve, but that the ions would be kept inside the protective film and would produce there a protection which is at present not understood. For this it would be necessary to have a thick protective layer. Cobalt does not give alloys with lead [16]. To get cobalt into lead alloys we made use again of the principle of selecting a third component, giving alloys with both components. Tin appeared to be a very successful component, forming alloys with cobalt, silver, and lead and should facilitate the uniform distribution of both cobalt and silver in the lead: apart from this tin is a metal, the hydrolysis product of whose sulfate should give a compact and thick film on the anode. The results of testing the stability of single quaternary alloys of lead-silver-tin and cobalt are included on Table 5.

Table 5

Loss of Weight of, and Weight of Protective Film on, Anodes of Lead Alloyed with Silver, Barium, Strontium, Arsenic, Tin and Cobalt in the Electrolysis of 2 N H_2SO_4, Containing 100 mg/liter of Cl^- at 400 amp/m^2

No. of alloy	Pb	Ag	Ba	Sr	As	Sn	Co	167	334	500	678	845	Weight of protective film at the end of electrolysis (in g/m^2)	Loss of weight calculated on metallic lead
								Loss of weight (g/m^2) after (hours):						
2	99.0	1.0	—	—	—	—	—	70	355	555	725	—	230	1175
51	98.4	1.0	0.5	—	0.1	—	—	—	—	—	197	—	918	1115
52	98.8	1.0	0.1	—	0.1	—	—	—	—	—	580	—	630	1230
50	98.0	1.0	—	1.0	—	—	—	—	—	—	550	—	640	1290
79	99.4	0.5	—	—	0.1	—	—	—	—	—	470	—	720	1190
53	98.5	0.5	—	—	—	1.0	—	143	398	568	710	—	230	930
54	94.5	0.5	—	—	—	5.0	—	153	170	320	450	570	680	1200
63	98.68	1.0	—	—	—	0.3	0.02	0	20	34	46	—	780	800

The data in Table 5 are very characteristic because they demonstrate that with almost identical true weight losses of the anodes in metallic lead (apart from Alloys Nos. 53, 54, and 63 which are more stable) the weight of the protective films on the different anodes was very different. Arsenic clearly promotes the formation of compact films. Tin increases the stability and gives thick films even at a reduced quantity of silver. The favorable action of tin on the stability of lead-silver anodes confirms again our initial idea about the desirability of introducing a third component giving solid solutions both with lead and with silver. Particularly interesting are the results of testing the quaternary Pb-Ag-Sn-Co alloy which was more stable than all those tested before [18]. The protective film obtained on this alloy was particularly massive and compact; no ions of cobalt could be detected in the solution around the anode; in accordance with our supposition the protective action of cobalt was developed inside the thick protective film.

Later special experiments were conducted to determine the quantity of lead going into solution and on to the cathode with anodes of different composition, i.e. with protective films of different thicknesses and densities.

Table 6
Quantity of Lead, Going into Solution and to the Cathode (Totalled) with Anodes of Lead and its Alloys in the Electrolysis of 2 N H_2SO_4 at 400 amp/m^2 for 100 Amp.Hrs

Alloy Nos.	Composition of anode alloy (in %)							Cl content of electrolyte (in mg/liter)	Quantity of lead (in g) going into solution and onto cathode in 100 amp.hrs (67 hours) electrolysis
	Pb	Ag	As	Ba	Tl	Sn	Co		
1 {	100.0	---	---	---	---	---	---	None	0.095
	100.0	---	---	---	---	---	---	100	0.103
2 {	99.0	1.0	---	---	---	---	---	None	0.033
	99.0	1.0	---	---	---	---	---	100	0.030
29	97.0	1.0	---	---	2.0	---	---	100	0.026
39	99.4	0.5	0.1	---	---	---	---	100	0.012
51 {	98.4	1.0	0.1	0.5	---	---	---	None	0.011
	98.4	1.0	0.1	0.5	---	---	---	100	0.007
56	98.9	1.0	0.1	---	---	---	---	100	0.009
63	98.68	1.0	---	---	---	0.3	0.02	None	0.003

For this purpose the anodes were placed in diaphragms of dense vinyl fabric ("Kalmuk") to eliminate the precipitation of slime into the solution; the cathodes were of aluminum. After the electrolysis the (combined) quantities of lead were determined in solution and at the cathode (dichromate-iodide method). The original electrolyte was 2 N sulfuric acid. The results of the investigation are shown in Table 6.

From these results it is seen that the most stable (apart from Alloy No.63) anodes (e.g., No. 29) put more lead into solution than the less stable ones (Nos. 39, 51 and 56). This indicates the effect of thick and compact protective films, formed as a result of the presence of As and Ba in the Alloys Nos. 39, 51 and 56.

Particularly interesting are the data relative to Alloy No. 63, which put the largest quantity of lead into solution, conditioned by the dense and thick protective film formed on it.

We confirmed by experiment the earlier assertion that covering the surface of cast lead with an electrolytic lead perceptibly increases the stability of the anode. For this purpose the surface of cast lead was covered with cathodic lead by electrolysis in the following solutions: normal fluosilicic, at a c.d. of 120 amp./m^2 [19], and in a sulfamic acid one with a c.d. of 500 amp./m^2 [20]. From the first solution a coarse-grained deposit was obtained, and from the other a fine-grained one which was very compact. This dense deposit was not more stable under anode polarization in 2 N H_2SO_4 at 400 amp./m^2 than was cast lead. The deposit of lead from the fluosilicate solution decomposed 60% faster than cast lead under these conditions. This confirms the opinion of some authors about the importance of grain size for the corrosion resistance of lead [15]. Electrolytic deposits of lead were, of course, considerably less stable than alloys of lead with 1% of silver.

In view of the interest of various investigators in the electrolysis of sulfuric acid solutions at very high current densities, and at high acid concentrations, we made tests of anode stabilities of individual alloys at high c.d.'s, acid strengths and temperatures (Table 7).

Table 7
Loss of Weight of Anodes of Lead Alloys at High C.D's and High H$_2$SO$_4$ Concentrations

Alloy No.	Anode alloy composition (in %)					Acidity (N)	C.D. (in amp./m²)	Temp. (in °C)	Loss of weight (in g/m²) after electrolysis (amp.hours)			Weight of protective film (g/m²) after 300 a/h	Weight of slime (g/m²) after 300 amp. hours	Loss of weight calculated on metallic lead (g/m²) after 300 a/h
	Pb	Ag	Ca	Ba	As				100	200	300			
1	100.0	--	--	--	--	2	400	25	850	2040	3250	--	3060	---
						4	1000	35	1832	--	--	--	--	---
						6	10000	50	1381	2784	3521	45	4053	3564
2	99.0	1.0	--	--	--	2	400	25	169	416	760	280	420	850
						4	1000	35	175	592	1004	--	--	---
						6	10000	50	243	483	709	50	903	829
31	98.0	1.0	1.0	--	--	2	400	25	+67	10	86	430	205	552
						4	1000	35	246	777	1261	--	--	---
						6	10000	50	244	443	812	84	1089	1020
52	98.8	1.0	--	0.1	0.1	2	400	25	109	310	520	470	595	920
						6	10000	50	276	305	695	40	759	695

Examination of the data in this table shows that going from the usual to higher current densities with a corresponding elevation of the acidity and temperature does not produce any notable lowering of the stability of anodes of lead or of its alloys with silver, arsenic or barium. Alloy No. 31, containing Ca, decomposes more extensively at high current densities. At very high current densities the weights of the protective films on the anodes are in all cases small, i.e., they are thin. This is evidently because under these conditions the layer of lead peroxide is more porous and is more easily detached by the strong evolution of oxygen at the anode. The quantity of anode slime in all cases considerably increases in going to very high current densities; anodes containing arsenic give the least percentage increase in quantity of slime. In all cases average current densities at average acid strengths and temperatures produce a considerable lowering of the stability of the anodes as compared with small and high values of the c.d. The explanation of this may be sought in the distribution of current between the surface and the interior of the anode, covered with a protective film.

In this section of our work we do not dwell on the clarification of the mechanism of the protective action of the individual alloying components in lead anodes and only draw conclusions based on the results of the determination of the anode stabilities of various lead alloys in terms of the loss of weight of anodes during the time of test.

SUMMARY

1. It has been established that all the anodes which show greater stability on electrolysis in sulfuric acid solutions contain around 1% of silver. The anode stability of Pb-Ag alloys is considerably raised by adding a third component to the alloy, such as Tl and Sn, which give solid solutions with the Pb and the Ag, and facilitate the more regular distribution of the Ag in the Pb. The most stable is the quaternary alloy of Pb-Ag-Sn-Co, in which the protective action of Co ions, noted earlier, is developed inside a protective film. The electropositive metals Au and Hg not only do not raise the stability but even lower it. The protective

action of Ca and Se in alloys is only temporary.

2. Tin and also calcium, barium, and strontium, giving low solubility compounds with sulfuric acid, facilitate the formation of thick protective films on the anode. The presence of small quantities of cobalt in Pb-Ag-Sn alloys induces a considerable increase in the compactness of the protective films. The beneficial effect of a certain quantity of As in anode alloys on the compactness of the protective film has been demonstrated. Chloride ions, present in small quantities in the electrolyte, cooperate in increasing the compactness of the film on lead-silver anodes.

3. It has been shown that the quantity of lead going into the electrolyte (and also onto the cathode) depends on the compactness of the protective film on the anode, which prevents the diffusion of the divalent lead ions and has no direct connection with the grain size of the metal.

4. Experiments on the use of cast lead covered with a deposit of electrolytic lead showed that the rate of solution of the lead on the anode depends to some degree on the grain size of the metal.

5. Experiments on the use of elevated current densities and at the same time higher acidities and temperatures of the electrolyte showed that the stability of lead-silver alloys was only little diminished by these factors; the quantity of anode slime and the thickness of the anode film were both increased.

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INVESTIGATION OF THE HYDRODYNAMICS OF PACKED RECTIFYING COLUMNS

V.V. Kafarov and L.I. Blyakhman

Packed rectifying columns are widely used both in industry and in laboratory practice.

In a previous investigation [1] we showed that the separating efficiency of a packed rectifying column depends on the hydrodynamic conditions of its operation. Hence a knowledge of the way in which hydrodynamics governs the operation of such a column appears to be absolutely necessary.

However, an investigation of the hydrodynamic basis for the working of such a column has not been carried out. The investigations of the hydrodynamics of packed columns described in the literature relate only to the movements of the liquids and gases in scrubbing processes, which do not completely correspond in character to the flows of streams of liquid and vapor in packed rectifying columns.

While not denying the similarity between the operation of packed absorbent and rectifying columns, some specific peculiarities of the hydrodynamics of rectifying columns must be borne in mind.

1) In a rectification column there is interaction between saturated vapor and boiling liquids; in absorption columns there is interaction between gases and liquids, far from their liquefaction or boiling points.

2) In rectification columns there is continuous boiling of liquid and condensation of vapor. In absorption columns such transitions from one state to another do not occur.

3) In rectification columns there is no continuous flow of liquids and vapor. An element of volume of vapor does not pass up the whole height of the column, but after attaining a certain height, condenses and then runs down again in the form of liquid. Above this also fresh vapor is formed, as a result of the heat of condensation. The same applies to the liquid. In contrast to this, in absorption columns, gas and liquid flow unchanged through the whole height of the column, and show no tendency to go over from one phase to the other.

4) In rectification columns there is always a considerable change of the composition of the liquid and vapor up the column, and, consequently, the physico-chemical properties of liquid and vapor are a function of the height. In absorption columns the physico-chemical properties of liquid and gas usually do not change much with height.

5) In rectification columns it is often necessary to deal with considerable changes in the rate of flow as the column is ascended, which is explained both by variations in the differences in density of liquid and vapor in different sections with height, and by differences in the heat of evaporation. In absorption columns, the change in the rate of flow with height is usually not great.

In devising experiments for the study of the hydrodynamics of packed rectification columns, our objective was to find out to what extent the hydrodynamics of such columns differ from those of absorption columns and whether the data obtained for absorption columns could be used for calculations on rectification columns, and to what extent the former need correction for this purpose.

The investigation of the hydrodynamics of packed rectification columns was carried out in the following stages: a) determinations of the hydrodynamic resistance of the non-irrigated packing; b) determination of the hydrodynamic resistance of the irrigated packing; c) determination of the limits of loading of the column for vapor and liquid; and d) determination of the hydrodynamic resistance of the packing at its limits of loading for both vapor and liquid.

EXPERIMENTAL

<u>Description of the experimental apparatus.</u> Our investigation was made on a laboratory model column, as depicted in Fig. 1.

Fig. 1. Layout of apparatus. For explanation of numbers see text.

The experiments were carried out in a glass column 10 with an internal diameter of 28.4 mm; the packing, of glass rings, was 1100 mm high. The packing was supported on a flat glass spiral, which was placed on projections in the walls of the column. The free cross-section of this support was larger than the free cross-section of the packed part of the column.

To create adiabatic conditions of operation in the column so as to prevent condensation on the walls the column was surrounded by a jacket formed of two concentric glass tubes 9 and 8, whose diameters were, respectively, 45 and 70 mm. Between the inner and the outer tube two electrical heating elements were located 7, permitting the creation of three temperature zones up the column. The temperature in the space between the column and the outer tube was measured by means of two thermocouples 12, placed in the upper and lower zones. The ends of the thermocouples were connected to a galvanometer, set up on the control panel. The temperature in the upper and lower zones of the heating jacket was maintained so as to have the same temperature gradient inside the jacket, as in the column during operation. The construction of the jacket described was such that, apart from maintaining adiabatic conditions inside the column, it permitted visual observation of the streams of liquid at all heights of the column.

A round-bottomed three-necked flask 1 of capacity 2 liters, was used as a boiler; it led directly into a reflux condenser 3, for adjusting the pressure. Around the exterior surface of the flask an electrically heated element of 1500 watts was arranged. The rate of evaporation was regulated by means of a rheostat and ammeter on the control panel. The rate was controlled by means of two meters 4 and 14, one of which was located below the packing, and the other above it. The lower meter 4 consisted of a graduated vessel with a sealed-in internal tube, over the covered end of which was placed a deflecting cap. The vapor, coming out of the flask, passed into the interior tube
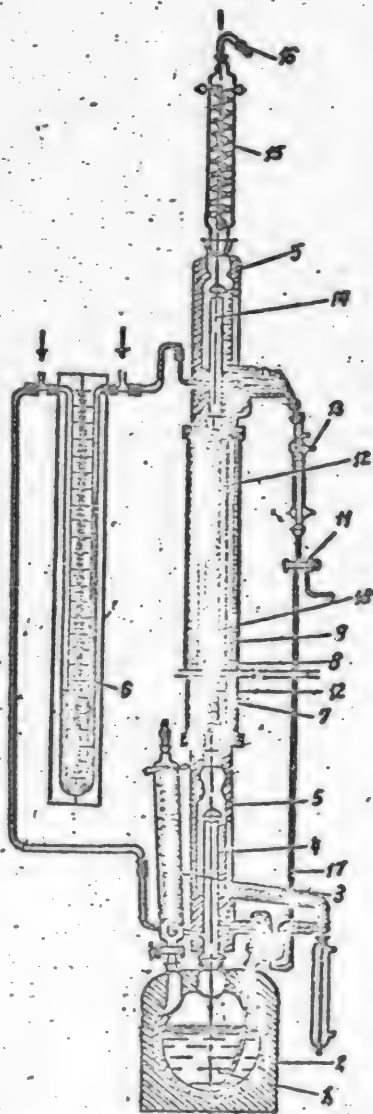
and thence into the packing, but the liquid trickling down the packing passed into the space between the internal and external tubes. The external tube was provided with divisions for noting the volume of liquid trickling down. The liquid was led out of the lower part of the wide tube and, passing through a three-way tap and a liquid seal, returned to the flask. The meter also had a side tube connected to a differential manometer 6. The upper meter 14 was of similar construction to the lower one, but had two one-way taps for measuring the quantity of liquid and for regulating the bleed-off of distillate.

The bleed-off of distillate was controlled with the aid of a graduated vessel 3, provided with a condenser. The liquid bled off as a distillate was returned to the boiler via the glass tube 17, provided with a liquid seal.

A reflux condenser, 15, was connected directly to the upper meter, 14, and the upper end of this condenser led into calcium chloride tube, 16. The meters 4 and 14 were insulated with asbestos, 5.

The diameters of the connecting tubes and ground joints in the flask, 1, and the meters 4 and 14 were such that they presented a free cross-section for passage of vapor, larger than the free cross-section of the packed column.

Glass rings of the Raschig type served as packing rings. Their average linear dimensions, as determined by measuring 200, were 5.66 x 5.87 x 0.6 mm. The average surface of one of the rings was 2.055 cm^2. The quantity of rings filling up the column was calculated. The specific surface of the packing rings was calculated making allowance for the surface of the column's walls. The volume of the packed part of the empty column was determined by filling it up with water. The rings were inserted dry, and were shaken to make the filling compact. The mean free cross-section of the packing, numerically equal to the free volume, was determined by filling up the column containing the packing with water.

Determination of the hydraulic resistance of the non-irrigated column. To do this a liquid of definite composition was placed in the flask. Afterwards the heaters for the flask and the jacket were switched on. The temperature in the upper part of the column was maintained, by means of the jacket, at a few degrees above the boiling point of the liquid in use and was identical at all heights of the column.

The liquid was brought to the boil. To ensure uniform boiling, glass wool was placed in the flask. The vapor from the flask passed through the lower meter into the column, and then, passing through the upper meter, condensed in the reflux condenser, and ran back as liquid through the upper meter 14 and the graduated vessel with the condenser 13, through the glass tube 17 to the boiler.

The vapor rate was determined by measuring the quantity condensed in unit time. This quantity was determined by closing the tap on the meter 14 and noting on a stop watch the time required for filling up 10 ml.

The pressure drop experienced by the vapor in passing through the packing was determined with a water-filled differential manometer 6, one limb of which was connected to the lower meter 4 and the other to the upper 14.

Experiments to determine the hydraulic resistance of the non-irrigated column were made with the vapor of the binary mixture carbon tetrachloride-benzene, and also with the vapors of pure liquids — benzene, carbon tetrachloride, dichlorethane, ethyl alcohol, methyl alcohol and water.

Benzene, treated with sulfuric acid and twice redistilled, boiled at 80.1°, and had a density of $d_4^{20} = 0.8788$, and a refractive index $n_D^{20} = 1.5011$.

Dichloroethane was likewise twice redistilled and boiled at 83.5°, and had a density $d_4^{20} = 1.2523$, and a refractive index of $n_D^{20} = 1.4460$.

Carbon tetrachloride after double distillation had a boiling point of 76.6°, density $d_4^{20} = 1.5944$, and refractive index $n_D^{20} = 1.4592$.

Ethyl alcohol (90 wt. %) boiled at 78.4°, had a density $d_4^{20} = 0.8183$ and a refractive index of $n_D^{20} = 1.3602$.

Methyl alcohol after redistillation had a b.p. of 64.7°, a density of 0.7922 and a refractive index $n_D^{20} = 1.3285$.

For comparison, experiments were carried out in air. In these experiments air was fed into the flask; the quantity of air was measured at the inlet and outlet of the condenser by means of a gas-meter. The temperature of the air at inlet and outlet was also measured. In all experiments the fall in pressure at different vapor rates was measured. The measurements were carried out after attaining a completely steady state, as shown by attaining a constant pressure drop.

The value of the pressure drop was expressed in kg/m^2 (mm water column) for a 1 meter height of packing. The vapor rate v_0 was calculated for the entire section of the column, not filled with packing, and was determined from the relation

$$v_0 = \frac{V \cdot \gamma_1}{60 \cdot \gamma_v \cdot f \cdot 10^6} \ m/sec., \qquad (1)$$

where V is quantity of condensed liquid, measured with the upper meter (in cm^3/min); f is the cross-section of the column (in m^2); and γ_1 and γ_v are the densities of the liquid and vapor at the boiling point (in kg/m^2).

The relation between the pressure drop and the vapor rate is plotted logarithmically in Fig. 2. Examination of this plot shows that the relation between these two quantities is linear, with a discontinuity. The straight lines are distributed on the graphs corresponding to the density of the vapor. The greater the density of the vapor, the higher the straight line and, consequently, the greater is the fall in pressure for the same vapor rate.

The discontinuity on the straight lines corresponds to a change of hydrodynamic condition. Above the discontinuities all the straight lines have the same slope. Below them (at low vapor rates) the slopes of the straight lines are different and are not identical. It should however be noted that in this range of change of the vapor rate the relative experimental error increases, since the accuracy of the calculation of the evaporation rate is of the order of 0.5 cm^3/min., so that an error of 20% may arise in a rate of evaporation of 2.5 cm^3/min., whereas when the rate is 50 cm^3/min., it will be only 1%.

The dependence of the pressure drop on the vapor rate for a given vapor may be expressed in the form

$$\Delta P = a v_0^n \qquad (2)$$

The index n, determined by the slope of the straight lines above the discontinuities, is 1.55. The value a depends for a given packing on the properties of the vapor. For the straight lines obtained the value of a varies from 125 for water vapor to 600 for carbon tetrachloride vapor.

To generalize the results of investigation, the experimental data obtained were worked over so as to give a relation between the resistance coefficient, and the Reynolds number Re, the latter being calculated from the formula

$$Re = \frac{4 \cdot v_0 \cdot \gamma_v}{g \cdot \mu_v \sigma}, \qquad (3)$$
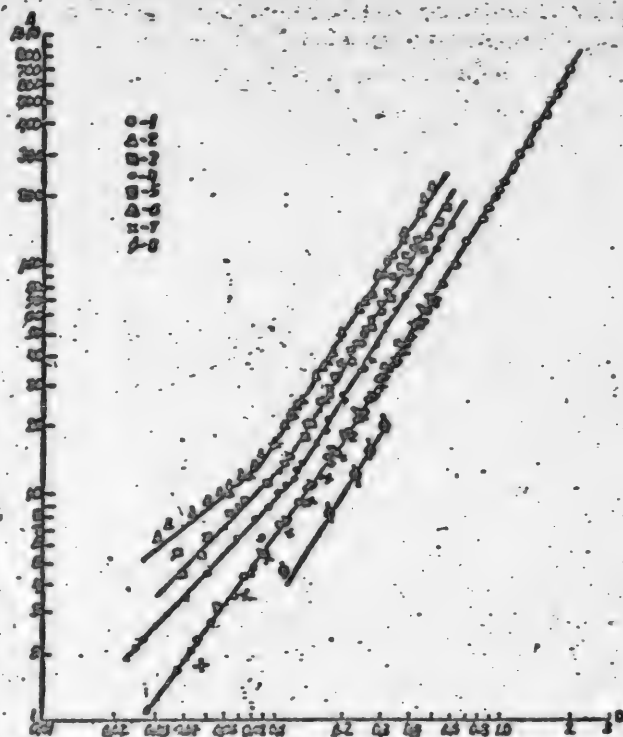
Fig. 2. Dependence of the hydraulic resistance of the non-irrigated packing on the vapor rate.
A – pressure drop, ΔP (in mm H_2O); B – vapor rate w_0 (m/sec).
1 – air; 2 – CCl_4; 3 – $C_2H_4Cl_2$; 4 – C_6H_6; 5 – CCl_4 – C_6H_6;
6 – C_2H_5OH; 7 – CH_3OH; 8 – H_2O.

and the coefficients from the formula:

$$\xi = \frac{8 \cdot \Delta P \cdot g \cdot F^3}{w_0^2 \cdot \gamma_v \cdot \sigma \cdot l} \qquad (4)$$

where σ is the specific surface area of the packing (in m^2/m^3), F is the average free cross-sectional area of the packing (m^2/m^2), μ_v is the viscosity of the vapor (in kg.sec/m^2), l is the height of the packing (in m), and g is the acceleration due to gravity (m/sec^{-2}).

The surface area of the walls of the column is included in the specific surface area of the packing.

The densities and viscosities of vapor and liquid at corresponding temperatures were taken from handbooks [2-4].

A generalization of the experimental data is presented in Fig.3, where the abscissa is divided in units of Reynolds number, and the ordinate in units of the coefficient of resistance.

It follows from Fig. 3 that the experimental points for the saturated vapor of different liquids, and also those for air, are grouped around one straight line, having two discontinuities. These occur at Reynolds numbers of 80 and 400. They correspond to a change in the character of the vapor flow through the packing. On the figure it is evident that there are three different flow regimes. Expressing the dependence of the resistance coefficient on the Re analytically, we obtain for these three regimes the following equations:
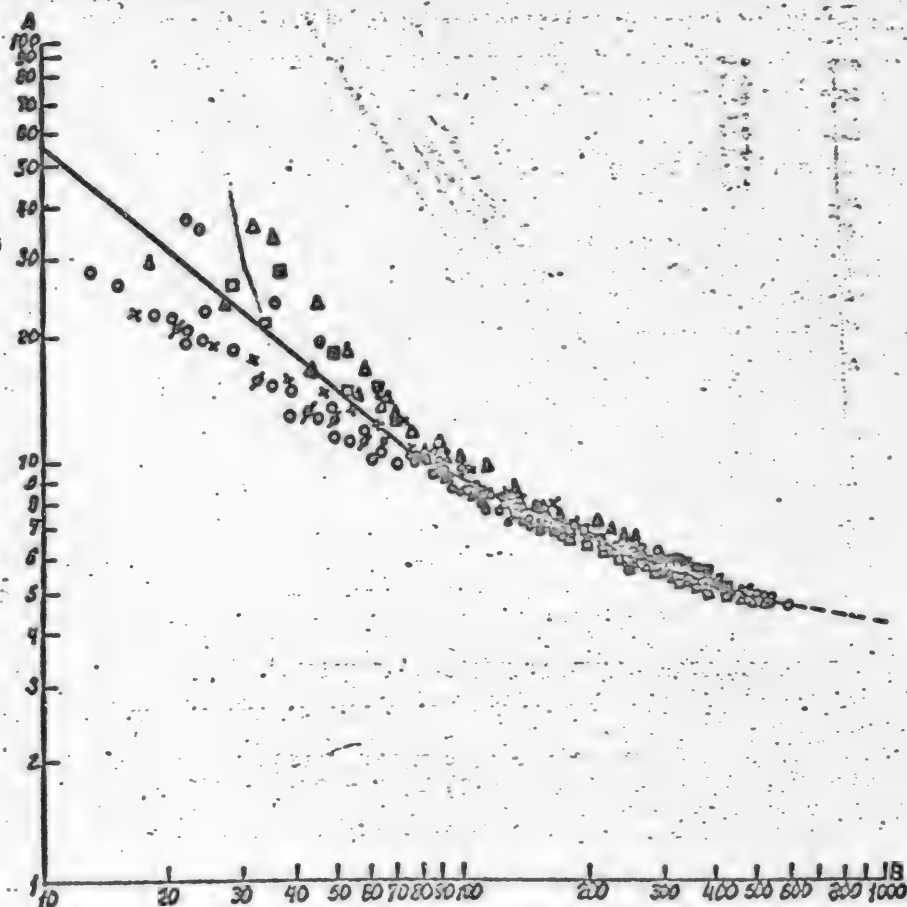
Fig. 3. Dependence of the resistance coefficient on Reynolds number.
Designation of the points the same as on Fig. 2.

$$\text{for the region } Re < 80 \quad \xi = \frac{400}{Re^{0.85}} \tag{5}$$

$$\text{for the region } 80 < Re < 400 \quad \xi = \frac{70}{Re^{0.45}} \tag{6}$$

$$\text{for the region } Re > 400 \quad \xi = \frac{16.5}{Re^{0.2}} \tag{7}$$

It should be observed that the experimental points for air also lie on
the lines common for all vapors. From this it can be asserted that in non-
irrigated, packed columns the dependence of the hydraulic resistance on the
character of the flow is identical for all saturated vapors, and also for
gases. Hence in the calculation of the hydraulic resistance of unirrigated,
packed columns for saturated vapors it is quite sufficient to use the
experimental data for air, corrected for the corresponding physical properties
of the vapor.

For comparison, our experimental data on hydraulic resistance of packings
of glass-rings for vapors of different organic liquids and air are plotted in
Fig. 4 along with those of other investigators for the hydraulic resistance of
packings of ceramic rings, used by Zhavoronkov [5], and packings of spheres used
by Fedorov [6], from which it follows that the dependence of the resistance co-
efficient on Re for glass and ceramic rings is identical for values of Re above
400. For Re less than 400, the resistance for glass rings is higher than that
for ceramic ones. However, careful examination of the data on the basis of

which Zhavoronkov drew his conclusions, shows that the divergence between our data and his is appreciable only at Re's less than 150, at which Zhavoronkov tested packings of porcelain rings with an external diameter of 6.27 mm, an internal diameter of 4.02 mm and a height of 10.2 mm.

It is clear that packings of such tubular rings cannot be identical with packings composed of rings of diameter equal to their height. At the same time even the direct determination in each separate case of such generalized characteristics of a packing as the free cross-sectional area (from the value of the free volume) and specific surface, do not yield single-valued results for a given filling. This can be related to two extreme possibilities for a packing of rings:

1) All the rings lie horizontal, i.e. the axes of all the rings are perpendicular to the axis of the column; and 2) all the rings are vertical, i.e., the axes of all the rings are parallel to the axis of the column.

Assuming that at identical volumes the quantity of rings in one or the other attitude is identical, we can consider that both the free volume and the specific surface of the packing are identical for both these cases. At the same time it is quite clear that the hydraulic resistance cannot be identical in both cases.

For a random packing of geometrically similar objects, for example ceramic rings with diameter equal to their height, the elements of the packing can be disposed in any attitude between the two extremes noted, and according to the theory of probability, for a sufficiently large number of elements, there will always be a definite relationship between the quantity of rings disposed horizontally, vertically, and at other angles. Correspondingly, experiments performed on identical, geometrically similar packings, usually give concordant results.

From what has been said it follows that as such generalized characteristics as the specific surface and the free cross sectional area, numerically equal to the free volume, do not completely characterize a given packing, the divergence between our data and those of Zhavoronkov can be explained by the absence of complete geometric similarity between our packing and his.

The difference in the dependences of the resistance coefficient on Re for packings of rings and spheres can be explained in the same way.

Determination of the hydraulic resistance of irrigated packings. Experiments on the determination of the hydraulic resistance of irrigated packings were carried out in the apparatus described above, with the following liquids and binary mixtures: benzene, dichloroethane, carbon tetrachloride, methyl alcohol, ethyl alcohol, benzene-dichloroethane, and carbon tetrachloride-benzene.

In contrast to experiments on the hydrodynamics of packed absorbers, in which it is usual to determine the dependence of the hydraulic resistance on the gas rate for a constant irrigation density or on the irrigation density at a constant gas rate, in our experiments to determine the hydraulic resistance in packed rectification columns, the liquid and vapor rates changed simultaneously, but in such a way that the mass rates of liquid and gas vapor remained unchanged (L/G const). This is because, in rectification the reflux ratio R is important, this being the ratio of liquid returned to the column, to the liquid extracted from the column as distillate per unit of time. Comparison of the results can be made only with R = const.

From this it follows that the ratio of the mass flow rates should also be made under the condition of $\frac{L}{G}$ = const.

In experiments on the determination of the hydraulic resistance of irrigated columns, the following were measured: the quantity of liquid irrigating the column; the quantity of liquid, extracted as distillate; the pressure drop through the packing; and the hold-up capacity of the column (dynamic).

The quantity of liquid irrigating the packing, was measured as follows. The tap on the lower meter was closed, and the time was noted on a stop watch, in which 10 ml of liquid collected. The quantity of liquid withdrawn was controlled by the cock on the upper meter and in the same way, using a stop watch, the time taken to collect 5 ml of liquid in the graduated vessel was noted.

The vapor rate in the column was calculated from the quantity condensed in the upper reflux condenser per unit of time. This quantity was equated to the total quantity of liquid irrigating the packing and withdrawn as distillate. A check measurement was made by measuring the quantity of liquid, condensing per unit of time in the upper condenser with the help of the upper meter.

In the performance of the experiments on the hydraulic resistance of packed irrigated columns, the liquid and vapor densities were taken at an average concentration of liquid in the column, for calculating the liquid and vapor rates. For determining the leading limits of the column for vapor and liquid the vapor rate was calculated on the cross-section at which flooding was first visually observed.

The hold-up capacity of the column, by which we mean the quantity of liquid held up in the packing during the time of operation, includes the liquid held up by capillary attraction (static hold-up capacity depending only on the physical properties of the liquid and the dimensions and material of the packing)and of the quantity of liquid moving against the vapor (dynamic hold-up capacity, depending not only on the physical properties of the liquid and the dimensions of the material of the packing, but also on the loading of the column with liquid and vapor).

For measuring the static hold-up capacity of the column the previously dried out packing was washed out with a definite quantity of the liquid under examination, sufficient to wet the whole packing. The temperature in the column was maintained close to the boiling point of the given liquid. After three minutes, the quantity of liquid which had flowed out was measured, and the difference between the quantity of liquid which had been poured into the packing, and that which had flowed out of it, was taken as the static hold-up capacity of the packing.

To measure the dynamic hold-up capacity of the packing the access of vapor to the column was prevented by closing the tap on the lower reflux condenser, so that the pressure drop fell to zero. The quantity of liquid flowing out of the packing in the course of three minutes was taken as the dynamic hold-up capacity of the packing.

Measurements were carried out successively in the following order: in the steady state the pressure drop was determined, and then the quantity of liquid irrigating the column was determined, along with the quantity of liquid withdraw Afterwards a check measurement of the quantity of liquid was made with the uppe meter. Since after this check measurement the running of the column had become somewhat disturbed, due to a short interruption of the irrigation of the column the measurement of the dynamic hold-up capacity of the column was made after restoring the original running conditions of the column (pressure drop check).

From observation of the flow of fluids in packed columns during rectification with complete reflux it was established that the following features of operation are characteristic:

At small evaporation rates, when the rates of flow are also small, the trickling liquid accumulates on the lower elements of the packing in the form of drops. When the drops attain a definite size, they come into contact with lower-lying elements of the packing or fall from the elements to which they are attached, to the lower lying ones. In this stage the generation of vapor does not change the visible character of the trickling of liquid.

When the rate of evaporation increases, the dropwise flow of liquid gradually gives way to streaming-film trickling. The movement against the direction of the vapor causes "jerky" trickling of the liquid films, which continuously increases as the vapor rate increases.

With further increase of the evaporation rate, the quantity of liquid in the packing starts to increase, and at a certain height of the column the liquid completely fills the whole free volume of the packing. At this point the flow of vapor changes from continuous to discontinuous, bubbles of vapor break through the filling of liquid and packing, as though they were emulsified in it. Such an emulsified layer of liquid grows upwards from the section at which emulsification starts to some definite height. If the rate of evaporation does not change, the height of the emulsified layer remains constant. Such a regime, when the liquid constitutes the completely continuous phase, and the vapor the discontinuous one, is quite stable. Small increases of the rate of evaporation increase the height of the emulsified layer considerably. Further increase of the rate of evaporation causes a layer of liquid to be formed above the packing, and does not disturb the counter movement of liquid and vapor. At greater heights the rate of evaporation induces an increase in the depth of the layer of liquid over the packing until the upper meter is completely flooded.

It should be remarked that the existence of a definite cross-section at which the generation of an emulsified layer occurs, was established by visual observation. Below this section no emulsification was observed.

The hydrodynamic condition corresponding to the emulsification of the liquid in the packing, at which the continuous flow of vapor became discontinuous, is reminiscent of the "plug-like" flow condition in smooth tubes, as analyzed by L. S. Axelrodt.

After emptying the packing out of the column, and filling it again by the same method, the point of formation of the emulsified layer was different, but emulsification began at the same evaporation rate as before changing the packing. In this case also no emulsification was observed below the new boundary.

In order to get an emulsification of the liquid by the vapor, uniform at all heights, which would be of special interest for experiments on mass transfer, we repacked the packing again. During this operation some glass rings of smaller dimensions than the rest of the packing were placed directly on the support, so that the free cross section there would be diminished; the objective was to get the emulsified layer formed on the support itself. With such an arrangement of the packing, emulsification of the liquid started directly on the support itself, at a somewhat lower flow rate than in the previous case.

It was quite clearly seen by visual observation that the boundary at which emulsification occurred was conditioned by the free cross-section of the packing (at liquid and vapor rates identical at all heights of the packing). In filling the packing into the column it is always likely that variations of the free cross sectional area fluctuates within the limits of 60-80%. Usually, the packing is characterized by the value of the free cross-sectional area of
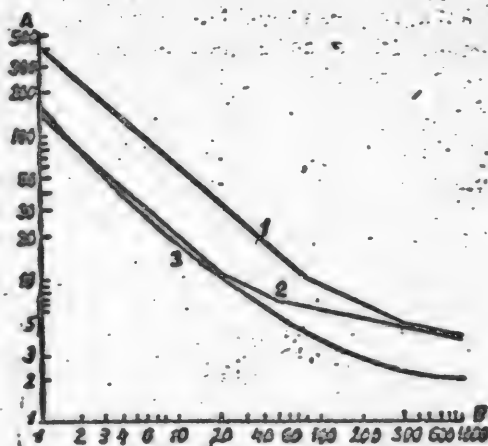
Fig. 4. Dependence of the resistance co-
efficient on Re for different packings.
1) Experimental data of the author, glass
rings; 2) Zhavoronkov's data, ceramic rings.
3) Fedorov's data, spheres.

Fig. 5. Flow rate profiles in
irrigated columns. A-A) Phase
boundary; 1) liquid; v) vapor.
For the conditions in the differ-
ent drawings, a-d, see text.

the packing numerically equal to
the free volume, which gives
only an average value of the free
cross-sectional area, as was ob-
served above in the analysis of
the hydraulic resistance of unirrigated columns. In our experiments it was estab-
lished that the emulsification of the liquid by the vapor began at the narrowest
section [1].

We did not observe any visual choking at a point of the kind usually described,
i.e., a reversed flow of liquid and its ejection from the column together with
the vapor. Our visual observations showed that at any definite rate of flow the
liquid in the narrowest cross-section begins to accumulate and gradually to fill
the entire volume of the packing, forming an emulsified layer. At this point the
vapor rate attains a value such that the friction at the phase boundary exceeds the
pull on the liquid due to gravity, so that the liquid at the phase boundary begins
to flow with the vapor (this relates only to the cross section indicated). The
main mass of the liquid continues to flow normally, i.e., countercurrent to
the vapor, as was established by measuring, in the lower meter, the quantity of
liquid trickling out of the packing when the packing became flooded. The quan-
tity of liquid withdrawn in unit time from the lower meter was somewhat less than
the quantity collected in unit time in the upper meter, when operating without
withdrawal of any distillate. The difference in quantity of liquid is accounted
for by the amount flooding the packing.

In Fig. 5 are shown schematic profiles of the liquid and vapor flow rates
in an elementary portion of the packing, similar to those deduced by L.S.Axelrodt
from a theoretical analysis of the flow of liquid and gas in smooth tubes with
irrigated walls.

At comparatively small linear vapor flow rates, the boundary layer carries
trickling liquid along with it (Fig. 5a). The existence of an internal vapor flow
in the opposite direction appears to be the source of eddies. As the rate of
evaporation increases, the linear liquid rate changes little by comparison with
the linear vapor rate. Hence, the rate profile changes with increased rate of
evaporation in such a way that there is a gradual reduction in the entrainment
of vapor by the liquid (Fig. 5b), and with further increase in the evaporation
rate the boundary layer of liquid begins to be entrained by the vapor stream,
(Fig. 5). Eddy formation penetrates now deep into the liquid. Considerable
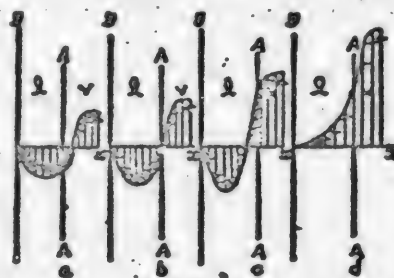
increase in the rate of evaporation can lead to a reversal of the direction of flow of the whole liquid layer (Fig. 5d). It should be said that such a scheme gives only an approximate idea of the flow pattern in elements, which do not exceed in size the dimensions of the elements of the packing itself.

At some constant rate of evaporation at which filling of the packing by the emulsified liquid begins, the column does not become completely flooded. The emulsified liquid fills the free volume of the packing to a definite constant height. The pressure drop through the packing attains a definite value, and also becomes constant. The conditions become stabilized, and identical values are obtained for measurements of the liquid with both upper and lower meters.

It seems to us possible to explain the phenomenon as follows. The accumulation of liquid in the packing leads to an increase in the absolute pressure in the column. The increase in pressure in turn raises the density of the vapor and diminishes its volume, and consequently its linear rate. The diminution in the linear vapor rate reduces the friction at the phase boundary. Thus the emulsified layer of liquid increases (in thickness) until the linear vapor rate is such that the quantity of liquid trickling down becomes equal to the quantity of vapor rising. If then the rate of evaporation increases slightly, the layer of emulsified liquid increases in thickness until the conditions become steady once again. The increase of the thickness of the emulsified layer in the packing results in the linear rate of the vapor remaining unchanged in spite of the increase in the rate of evaporation, from the point where the emulsified liquid layer appears until this layer is distributed throughout the whole height of the column.

The reversal of flow of the liquid and the complete cessation of the trickling down can occur, apparently, only at very high rates of evaporation, corresponding to a state where the pressure in the column, raised by the liquid, does not compensate the corresponding change of the linear vapor rate.

In Figs. 6a–d, the dependences of the pressure drop on the vapor rate at $\frac{L}{G} = 1$ ($R = \infty$) and $\frac{L}{G} = \frac{1}{2}$ ($R = 1$) are shown. For comparison the dependence of the pressure drop on the flow rate for an unirrigated column is shown.

As can be seen from the figures, the straight lines for the irrigated columns lie above those for the unirrigated ones and the pressure drop for the irrigated packing is greater, at one and the same rate, the higher the $\frac{L}{G}$ ratio. The dependence of the pressure drop on the vapor rate for an irrigated column is expressed on the graph by a straight line, having three discontinuities.

The first discontinuity on the straight lines for the irrigated packing corresponds to one on the straight line for the unirrigated packing and coincides with it at a somewhat smaller vapor rate. It can be taken that here the irrigation of the packing does not change the correlation established for unirrigated columns, and only causes an increase of the actual vapor rate. Hence this discontinuity can be explained by a change of the hydrodynamic conditions for the vapor flow.

The second discontinuity corresponds to the rapid increase of the pressure drop due to increased turbulence and to an increase of the quantity of liquid held up in the column. This can be seen at a glance from Fig. 7, in which the dependence of the dynamic hold-up capacity of the packing on the vapor rate for the carbon tetrachloride liquid-vapor system is shown.

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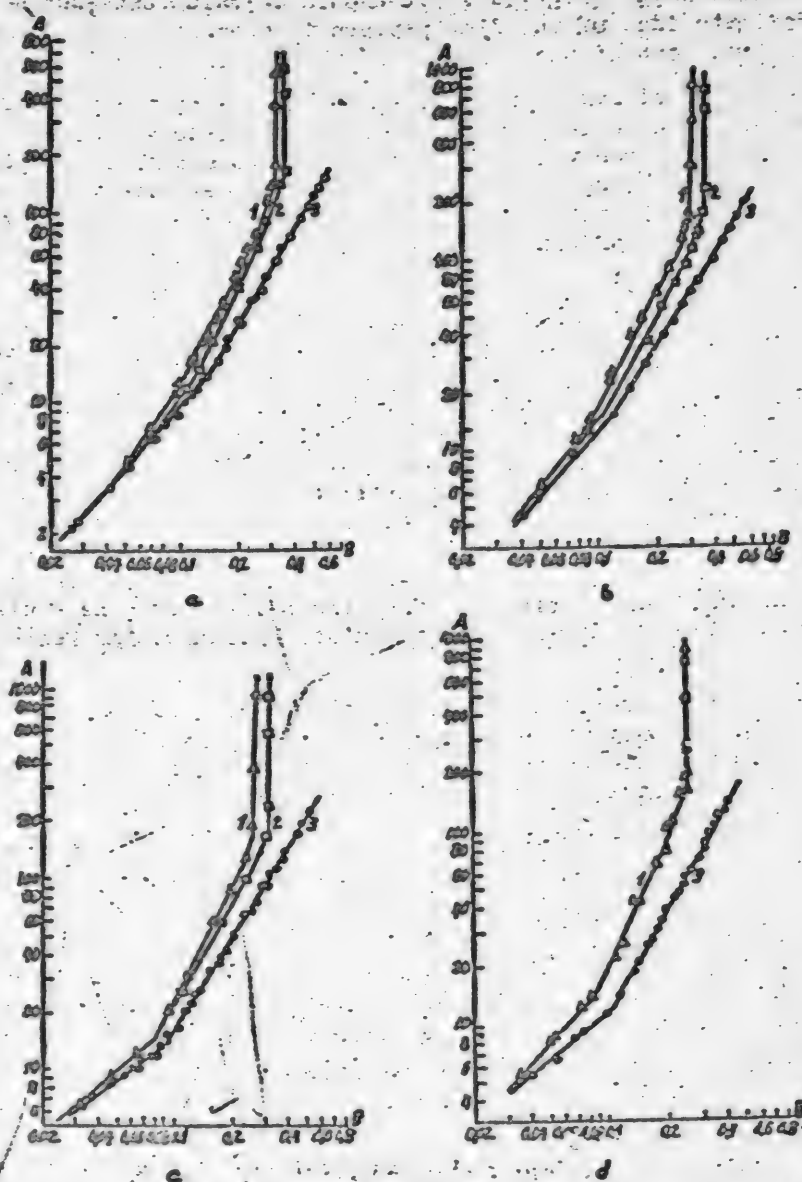
Fig. 6. Hydraulic resistance of an irrigated packing for some systems.

A — Pressure drop (in mm, H_2O/m); B — vapor rate y_0 (in m/sec).

$1 - \frac{L}{G} = 1$; $2 - \frac{L}{G} = \frac{1}{2}$; 3 — unirrigated packing.

a — benzene liquid/vapor; b — dichloroethane liquid/vapor; c — carbon tetrachloride liquid/vapor; d — carbon tetrachloride - benzene, liquid/vapor.

The third discontinuity relates to the initial appearance of the emulsified layer. Points above this discontinuity correspond to different heights of the emulsified layer.[1]

It should be noted that at different heights of the emulsified layer, right up to the distribution of this layer through the whole height of the packing, constant values of the pressure drop correspond with constant values of the flow rate. Thus, the emulsification condition is completely stable. Hence the condition of operation of packed columns, corresponding, on Fig. 6a-d, to points at the commencement of the appearance of an emulsified layer of liquid, is not the limiting one, as has been assumed up to the present time.[2] The column is quite stable under the conditions corresponding to all the points on
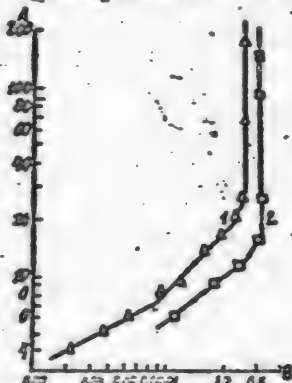
Fig. 7. Dependence of the dynamic hold-up capacity on the vapor rate. System: carbon tetrachloride, liquid vapor.
A – dynamic hold-up capacity of the packing (cm^3); B – vapor rate, $\underline{v}_0$ (m/sec) Designation of the curves the same as in Fig. 6.
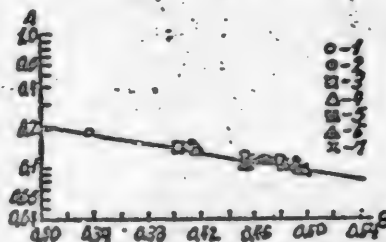
Fig. 8. Limiting throughputs of vapor and liquid in a packed rectification column.

$$A \sim \underline{v}_0^2 \cdot \left(\frac{\sigma}{g\Gamma^3}\right) \cdot \frac{\gamma_v}{\gamma_1} \cdot \mu_{\underline{1}}^{0.16},$$

$$B \sim \left(\frac{L}{G}\right)^{1/4} \cdot \left(\frac{\gamma_v}{\gamma_1}\right)^{1/8}$$

1 – Benzene-dichloroethane; 2 – benzene; 3 – dichloroethane; 4 – carbon tetrachloride; 5 – carbon tetrachloride-benzene; 6 – methyl alcohol; 7 – ethyl alcohol.

the straight line, above the point of commencement of emulsification right up to the distribution of the emulsified layer through the whole height of the packing. Further increase in throughput of vapor and liquid leads to an accumulation of the liquid over the packing, which does disturb the normal operation of the packed column.

As the flow rate only changes very little over the whole of the emulsification region, which corresponds to little change in the output of the column, the vapor and liquid throughputs, corresponding to the point of commencement of emulsification, may be taken with sufficient accuracy for practical purposes to be the limiting output of the packed column, bearing in mind, however, that a working condition, that of emulsification, does exist above this point.

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[1] The figure shows the linear vapor rate calculated from the quantity of condensed liquid, the pressure in all experiments being taken as atmospheric. Hence the line of dependence of the pressure drop on the vapor rate is not strictly vertical, but has a definite slope.
[2] This point has been defined as the "flooding point" or as the choking point.

To establish the quantitative relationship between the parameters defining the regime at which the emulsification of the liquid in the packed rectification column commences, we plotted our experimental data in terms of the coordinates

$$\left[\left(\frac{L}{G}\right)^{\frac{1}{4}} \cdot \left(\frac{\gamma_v}{\gamma_1}\right)^{\frac{1}{8}}\right] - \left[\frac{\sigma}{gF^3} \cdot \frac{\gamma_v}{\gamma_1}\mu_1^{0.16} v_0^2\right]$$. The convenience of this is that a linear plot is thereby obtained. Apart from this, since in the rectification column the quantity $\frac{L}{G}$ changes only within definite limits, the whole region of its change is covered in these coordinates.

The results of working up the experimental results in this way are shown in Fig. 8, where the dimensionless parameter $\left[\left(\frac{L}{G}\right)^{\frac{1}{4}} \cdot \left(\frac{\gamma_v}{\gamma_1}\right)^{\frac{1}{8}}\right]$, has been plotted along one axis (abscissa), while the ordinate is divided logarithmically in units of the quantity:

$$\left[\frac{\sigma}{gF^3} \cdot \frac{\gamma_v}{\gamma_1} \cdot \mu_1^{0.16} \cdot v_0^2\right]$$

As can be seen from Fig. 8, the experimental points are grouped around a straight line. By expressing the analytic equation of a straight line in these coordinates, we obtain the following relationship between the limiting throughput of vapor and liquid in packed rectification columns and the variables involved:

$$\log\left[\frac{\sigma}{gF^3} \cdot \frac{\gamma_v}{\gamma_1} \cdot \mu_1^{0.16} \cdot v_v^2\right] = -0.125 - 1.75\left(\frac{L}{G}\right)^{\frac{1}{4}} \cdot \left(\frac{\gamma_v}{\gamma_1}\right)^{\frac{1}{8}} . \quad (8)$$

In Fig. 9, our experimental data is compared, for the conditions in a column corresponding to the commencement of emulsification, with the experimental data for choking of a packed absorption column [10]. The comparison demonstrates that this relationship, for the system (condensing vapor-boiling liquid) is analogous to that which holds for the system (liquid-gas), and both these relationships are expressed as straight lines parallel to one another on the graph. The loading of the packed rectification columns (line 2) corresponds to the commencement of emulsification, and is somewhat below that of packed absorption columns, corresponding to the beginning of choking (line 1). This can be explained by the different character of the interaction of vapor and liquid in a rectification column, compared with the interaction of gas and liquid in an absorption column, to which we referred above.

The pressure drop through the packing is the parameter from which the hydrodynamic condition in a packed column can be judged. This pressure drop depends not only on the physical properties of the vapor and liquid and the rate of flow, but also on the quantity of liquid held-up in the column, on the degree of turbulence in the flow, etc.

At the same time the measurement of the pressure drop through the packing in a rectification column not only does not present any difficulty, but is also most easily compared with other quantities, characterizing the hydrodynamic condition. The possibility of making a theoretical calculation of the pressure drop through the column is of considerable importance, in particular at the point at which emulsification commences, since this condition determines the output of the column.

For determining the pressure drop in the packing, we used a method described earlier [11].

absorption columns, suggested to us the possibility of utilizing the method proposed earlier [11] and thereby to extract, from our experimental data for the hydraulic resistance of irrigated and unirrigated packings, a relationship of the quantity φ to the throughput for a rectification column for vapor and liquid and to the physical properties of the liquid and vapor.

In Fig. 10 are presented the results of analyzing the experimental data on the hydraulic resistance of irrigated packings at rates of flow corresponding to the commencement of flooding of the packing — i.e. the point at which an emulsified layer of liquid appears.

In the figure the abscissa is divided in terms of $\Phi = \left[\left(\dfrac{L}{G}\right)^{1.8} \cdot \dfrac{\gamma_v}{\gamma_1} \cdot \left(\dfrac{\mu_1}{\mu_v}\right)^{0.2}\right]$ and the ordinate in terms of

$$\varphi = \left[\frac{\left(\dfrac{\Delta P}{1}\right)_{v-1}}{\left(\dfrac{\Delta P}{1}\right)_v} - 1\right]\left[\frac{1}{\left(\dfrac{L}{G}\right)^{1.8}\dfrac{\gamma_v}{\gamma_1}\left(\dfrac{\mu_1}{\mu_v}\right)^{0.2}}\right]$$

As can be seen from the figures, the experimental points lie on one straight line, whose equation in these coordinates is:

$$\varphi = 5.15\,\Phi^{-0.81} \tag{11}$$

Inserting the value of φ found into Equation 10, we obtain:

$$\frac{\left(\dfrac{\Delta P}{1}\right)_{v-1}}{\left(\dfrac{\Delta P}{1}\right)_v} = 1 + 5.15\,\Phi^{0.19} \tag{12}$$

or finally

$$\left(\frac{\Delta P}{1}\right)_{v-1} = \left(\frac{\Delta P}{1}\right)_v \left[1 + 5.15\left(\frac{L}{G}\right)^{0.342}\left(\frac{\gamma_v}{\gamma_1}\right)^{0.19}\left(\frac{\mu_1}{\mu_v}\right)^{0.038}\right] \tag{13}$$

SUMMARY

1. The movement of vapors through unirrigated packings has been investigated and a generalized relationship for the frictional coefficient in terms of Reynolds number has been deduced in the form:

$$\text{for } Re < 80 \quad \xi = \frac{400}{Re^{0.85}};$$

$$\text{for } 80 < Re < 400 \quad \xi = \frac{70}{Re^{0.45}};$$

$$\text{for } Re > 400 \quad \xi = \frac{16.5}{Re^{0.2}}.$$

2. It has been shown that the relationships obtained for the movement of vapors through an unirrigated packing are analogous to those for the movement of gases through unirrigated packings.

3. The movement of vapors through irrigated packings has been investigated.

The existence of an emulsification condition has been established, in which the highest linear vapor rate is attained and also the highest packing resistance is met with. It has been shown that the emulsification condition is completely stable.

4. An equation has been found describing the emulsification condition for a loading corresponding to the beginning of emulsification; this is:

$$\log \left[\left(\frac{\sigma}{g F^3}\right) \cdot \frac{\gamma_v}{\gamma_1} \cdot \mu_1^{0.16} \cdot v_v^2 \right] = -0.125 - 1.75 \left(\frac{L}{G}\right)^{\frac{1}{4}} \cdot \left(\frac{\gamma_v}{\gamma_1}\right)^{\frac{1}{8}}$$

and for determining the pressure drop at the commencement of emulsification, we have:

$$\left(\frac{\Delta P}{1}\right)_{v-1} = \left(\frac{\Delta P}{1}\right)_v \left[1 + 5.15 \left(\frac{L}{G}\right)^{0.342} \left(\frac{\gamma_v}{\gamma_1}\right)^{0.19} \left(\frac{\mu_1}{\mu_v}\right)^{0.038} \right].$$

5. It has been shown that the existence of differences in the character of the flows in absorption and rectification columns is the reason why the limiting throughputs in rectification columns are less than those for absorption columns.

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GENERALIZATIONS ABOUT THE CHEMICAL STRUCTURE OF PLANT CARBOHYDRATES[1]

A.M.Goldovsky

All-Union Institute for Research on Fats

In our first paper [1] we formulated generalizations about the chemical structure of all groups of substances entering into the composition of plants. For subsequent papers we set ourselves the task of working out, in succession, particular generalizations about the structures of important groups of plant substances. Such partial generalizations are evidently steps towards overall generalizations, but are in no sense ends in themselves.

In our second paper [2] we formulated generalizations about the chemical structure of plant fats. In the present, third, paper, structural generalizations are presented about another important group of plant substances, namely carbohydrates; these generalizations are based upon exhaustive studies of the numerous factors on which the structures of carbohydrates depend [3-8].[2]

The work of Sadikov should be mentioned here [9]; he made attempts to generalize the structure of plant carbohydrates: Sadikov's results were considered in formulating our generalizations.

Generalizations about the Structures of Simple Carbohydrates (Monosaccharides)

1. Monosaccharides are usually composed of unbranched carbon atom chains, which form, in conjunction with oxygen atoms, pyranose and furanose rings having cyclic hemiacetal tautomeric forms of monosaccharides, or else they maintain the aliphatic chain form in tautomeric forms with unclosed rings. At present only three monosaccharides are known with branched carbon chains, constituting exceptions to the rule formulated above: apiose (in the composition of the glucoside apiin in parsley), hamamelose (in the composition of hamamelitannin in the shrub Hamamelis virginica), and streptose (in the composition of an antibiotic streptomycin, produced by the actinomycete Streptomyces griseus).

2. The length of the carbon chain in monosaccharides is subject to certain limitations: the number of carbon atoms in plant monosaccharides usually does not exceed 6. Only a few exceptions to this rule are known: three ketoheptoses (in the plants Persea gratis, Sedum spectabile and in certain other varities of Sedum), in which the number of carbon atoms is 7; this may at present be considered the maximum number of carbon atoms for the carbon chain of a monosaccharide.

3. There is only one carbonyl group in the chain of a monosaccharide.

4. The distribution of the carbonyl oxygen atom in the molecule of a mono-

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[1] Paper III in a series dealing with correlations in the chemical structure of plant substances.

[2] We do not refer to the multitudinous experimental investigations on separate points of the chemistry of carbohydrates and restrict ourselves merely to references to the more important bibliographies on the biochemistry of plants and the most recent reviews on the chemistry of carbohydrates, in some way or another of relevance to the question of interest to us here.

saccharide is restricted.

a) On the one hand carbonyl oxygens are only bound to carbon atoms in positions 1 and 2[1], forming aldoses or ketoses (concerning the other end of the oxygen bridge in tautomeric cyclic forms, see below). Thus, in the tautomeric forms of aldoses, with a straight carbon chain the carbonyl (aldehydic) group takes the extreme position (1); in ketoses the ketonic carbonyl group occupies the next position, i.e., carbon atom 2.

b) The majority of the known monosaccharides contain the carbonyl oxygen bound to carbon 1; i.e., the extreme position of the carbonyl group (in the form of an aldehydic group) in a tautomeric form with an open chain. Thus plant pentoses are, apparently, aldopentoses; plant ketopentoses have so far not been discovered.[2]

Plant hexoses comprise a number of aldoses and only one ketohexose - fructose. However, it should be mentioned that this ketohexose is widely distributed in plants both in the free form (d-fructose), and in the combined state (in disaccharides, as saccharose; in trisaccharides, as raffinose, gentianose, melizitose; in tetrasaccharides, as stachyose; in polysaccharides, as fructosans, in particular inulin).

The second known natural ketohexose is d-sorbose, and is obtained from the juice of the rowan tree (Sorbus aucuparia); judged by the data available, it is a product of the oxidizing action of the bacteria Bact. xylinum on the d-sorbitol contained in these berries.

It should be noted that all the rare heptoses discovered up to the present (in contrast, for example, to the pentoses and to some extent the hexoses) are only ketoses.

c) The cyclic tautomeric forms of the carbohydrates, formed by participation of oxygen in ring formation, contain only six- or five-membered heterocyclic rings corresponding to amylene oxide or butylene oxide bridges (pyran or furan rings). Thus, the carbonyl oxygen atom, bound on one side with carbon 1 in aldoses, or with carbon 2 in ketoses, is bound on the other side with carbons 5 or 4 in aldoses or with carbons 6 or 5 in ketoses.

5. All the carbon atoms in the molecules of monosaccharides, except one, carry hydroxyl groups. Each carbon atom can carry only one such hydroxyl group. Thus, the repeated unit -CHOH- occurs in the molecule of monosaccharides.

6. The bonds between the carbon atoms in the carbon chain of monosaccharides are saturated ones.

7. The spatial configurations of the molecules of monosaccharides have certain limitations: not all the possible stereoisomers of monosaccharides are contained in plants, but only a few. In particular, it should be noted that the majority of monosaccharides in plants have the d-configuration and only a much

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[1]) Here and later on the numbering of carbon atoms follows the rule that the first is in aldoses the final carbon atom of the carbonyl group, and in ketoses, it is the final carbon atom, next to the carboxyl group; thus, the other terminal carbon atom in hexoses is labelled the sixth, and in pentoses the fifth. In all cases we use the abbreviation of referring to carbon atom 1 as carbon 1.

[2]) As far as is known to us, the only natural ketopentose is l-xyloketose, formed in the human organism during pentosuria (a special form of metabolic disorder).

smaller number have the l-configuration.

Generalizations about the chemical structure of derivatives of simple carbohydrates.

8. Plants contain, together with carbohydrates (more frequently in complex compounds) other compounds similar to carbohydrates in composition, (sugar alcohols, sugar acids, desoxy sugars, in particular methyl sugars, amino sugars) which can be converted to carbohydrates by simple chemical processes (reduction, oxidation, methylation, amination):

9. Sugar alcohols always contain one alcoholic hydroxyl group on each carbon atom. It is extremely probable that sugar alcohols are to a greater or lesser degree, always associated with sugars in plants. Individual plants contain very large quantities of sugar alcohols.

10. Sugar acids are usually associated with carbohydrates in plants, and are usually uronic acids. The characteristics of their structure are as follows:

a) Uronic acids usually contain six carbon atoms, since they are derivatives of the usual plant hexoses (d-glucose, d-galactose, d-mannose).
b) The uronic acids contain only one carboxyl group.
c) The position of the carboxyl group in a uronic acid is limited - it occupies position 6, i.e. carbon 6 enters into the composition of the carboxyl group.
d) Uronic acids contain the carbonyl group.
e) Uronic acids are usually present, along with monosaccharides, in complex polysaccharides; thus d-glucuronic, d-galacturonic, and d-mannonic acids enter into the composition of gums, mucilages and pectins. We note that d-glucuronic and d-galacturonic acids also enter into the composition of certain specific polysaccharide bacteria.

11. a) Desoxy sugars[1] met with in plants (usually in the composition of compounds) contain not more than one CH_2- group and one $-CH_3$ group (we are referring here to those groups, the carbon atoms of which enter into the basic carbon chain of monosaccharides).
b) The positions of the $-CH_2-$ and $-CH_3$ groups in desoxy sugars are restricted: the carbon atom of the group $-CH_2-$ can only be No. 2 (2- and 2,6- desoxy sugar); the carbon of the $-CH_3$ group can only be No. 6 (6-desoxy sugar, or as otherwise known, methylpentose or 2,6-desoxy sugar).

12. Amino sugars are only present in considerable quantities in the lower plants in mushrooms as chitin. They are not found in higher plants, with one exception, as far as we are aware: in the glucoside karakin, contained in the fruit of Corynocarpus laevigata, an amino sugar has been discovered whose structure has not been accurately established (assumed to be an amino glucose or amino mannose). The chitin of mushrooms, like that of animals, apparently consists of acetylglucosamine residues in which the acetylamino group ($-NH-CO-CH_3$) occupies the position of carbon 2. Judged by the data available at present the amino group in natural aminosugars can only be located on carbon 2.

Generalizations about the chemical structure of complex carbohydrates

13. In each plant there is a specific complex of carbohydrates:

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[1] Desoxy sugar can be considered as monosaccharides, in which one of the $-CHOH-$ groups, or the $-CH_2OH$ group, has lost an oxygen atom, as a result of which the $-CH_2-$ or the $-CH_3$ group is formed.

a) Monosaccharides in the free state (d-glucose and d-fructose are met with most frequently in the free state); and b) polymers of monosaccharides in different degrees of polymerization from disaccharides (and likewise in a number of plants tri- and tetrasaccharides) corresponding to two (and likewise three and four) monosaccharide residues up to high-molecular polysaccharides with numerous monosaccharide residues in the molecule. The basic regularities of the structure of polysaccharides will be further examined.

14. a) Complex polysaccharide molecules, as a rule, consist of repeated units, combined with one another in straight or branched chains by principal valencies (not excluding the possibility of the existence of interlocked chains).

b) The repeated units of polysaccharides may consist of: 1) one or more residues of monosaccharides of one type (for example araban or a similar hexosan, such as starch, cellulose, inulin, galactan, laminarin, etc.) or more than one type (e.g. araboxylan, galactomannan); 2) one or some residues of uronic acids - polyuronides (e.g. pectinic or alginic acids); 3) monosaccharides and uronic acids (e.g., gums, mucilages, pectins); and 4) amino sugars (chitin).

15. The individual units of the monosaccharides and their derivatives in complex polysaccharides are bound to one another only through oxygen atoms.

16. The generalizations about the position of the bond between residues of monosaccharides and their derivatives in polysaccharides are as follows:

a) Carbon 1 of one of the aldose residues always takes part in the bond between aldoses, while carbon 2 of one of the ketose residues always participates in the formation of the bond between ketoses.

b) In the polysaccharides of higher plants carbon 1 of one of the aldose residues is bound through the oxygen atom most frequently to carbon 4 of the other residue. Such a 1,4-bond exists, for example, in cellulose, amylose and amylopectin of starch, glycogen, xylan, mannans, pectins and many other polysaccharides. However, it is possible for the carbon 1 to be bonded to any other carbon of a monosaccharide residue. Such bonds are met with rarely in the polysaccharides of higher plants, (considerably more rarely than 1,4- bonds); usually they are found at the point of branching from the basic chain, though they may be in the basic chains. The 1,3- bonds (in arabogalactans of larch trees) and the 1,6- bonds (in the arabogalactans mentioned in amylopectin of starch, most probably at the branching points and in glucosans from the barley roots) should be mentioned. The "unusual" bonds mentioned are characteristic for a series of polysaccharides of individual groups of lower plants and microorganisms. Thus, we find the 1,2- bonds (yeast mannan), 1,3-(yeast mannan, yeast polyglucose, laminarin from the seaweed Laminaria cloustoni, agar from the seaweed Gelidium and other agarophites, carrageen, from the seaweed Chondrus crispus). The 1,5-(galactocarolose, extracted from certain forms of Penicillium molds). The existence of 1,1- bonds in the disaccharide trehalose should be mentioned, distributed in lower plants (mushrooms, yeast, molds); there is no data about the existence of 1,1- bonds in polysaccharides.

In all probability, the 1,4- bond is extremely characteristic of glucose residues, although these residues can be bonded in other ways (e.g, by the 1,3- bond in laminarin). It is to be supposed that galactose residues are bonded predominatly by 1,3- bonds (e.g., in the galactoarabans of higher plants, agar, and carrageen).

c) The carbon atom 2 of one of the ketose residues is usually bonded (through an oxygen atom) with carbon 1 or 6 of another residue in the known compounds of fructose (fructosans). Thus, in inulin, the bond 2,1- is repeated; in the fructosans from the leaves of the larch, the roots of Phleum pratense (phlein), in rice straw (Sakhalin) the 2,6- bond is found. However, this does not exclude the possibility of a bonding of carbon 2 with other carbons such as 1 and 6.

17. In complex carbohydrates, the molecules of which are constructed of unbranched chains of identical units bonded by main valencies, the bonds between all the units are usually of the same type, which is characteristic for the given carbohydrate. Thus, for example, in cellulose only bonds of the type β-1,4- are repeated between the units, while in starch amylose only bonds of the type α-1,4- are repeated, etc.[1])

18. In complex carbohydrates, where the molecules are constructed of branched chains, united by main valencies, it is possible to have bonds of several types. Thus, for example, in starch amylopectin there are bonds of two types: α-1,4- and α-1,6-, while in the yeast mannan the bonds α-1,2-, α-1,3- and α-1,6- are found. Thus it may be surmised that in these cases only one type of bond is repeated between the units in the basic chain (in agreement with the rule formulated above for polysaccharides with unbranched chains), and bonds of one or several other types are located at the points of branching and in the side chains. Thus it may be supposed that in the basic chain of starch amylopectin only α-1,4- bonds are repeated between the units, but that branching occurs through α-1,6- bonds; however, as far as we know, this has been in no way confirmed experimentally. There are different ideas about the disposition of the bonds of different types in yeast mannan, including the suggestion that 1,2- bonds are located in the main chains, and the 1,3- and 1,6- bonds in the side chains.

19. In the composition of some complex carbohydrates, inorganic elements may be present. The bonding of these elements can be different, in particular the following bond forms are possible: a) individual monosaccharide residues in complex carbohydrates can be esterified by mineral acids: phosphoric acid (in the polysaccharides of potato starch) or sulfuric acid (e.g. in the polysaccharides of fucus, in particular in agar). According to some ideas, the residues can even be esterified by silicic acid. As a rule only one hydroxyl of the given residue is esterified. Thus, from the hydrolysis products of potato starch glucoso-6-phosphate can be isolated. Thus, in the glucose residue, the primary alcoholic group of carbon 6 is esterified. In agar from red fucus (gelidium and other agarophites), in the terminal chains of l-galactopyranose residues, esterification by sulfuric acid has occured at carbon 4 (in carrageen from Chondras crispus; the galactopyranose residue is esterified by sulfuric acid at carbon 4 also). It is highly likely that it is the terminal monosacharide residue which is esterified, as happens in agar:

b) Mineral elements can form independent compounds either directly through the carboxyl group of the sugar acids, replacing the hydrogen of the carboxyl (thus, for example, the pectin acids are present as their calcium and magnesium salts, the complex carbohydrate acids of gums and mucilages are in all probability calcium, potassium and magnesium salts, the alginic acid in a number of seaweeds is a mixture of the free acid and its sodium, potassium and calcium and magnesium salts) or through bonding of the residues of carbohydrates with mineral acids,

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[1]) In all probability, in each given polysaccharide only α-or only β-glucosidic bonds are possible. This does not exclude the possible existence, in individual (probably rare) cases, of alternating bonds of different types in the polysaccharide chain. Thus, there is an indication of the existence of two types of bonds (β-1,3- and β-1,4-) in the polysaccharides of pneumococci of type III with unbranched chains, consisting of regularly alternating 1,3- and 1,4- bonds, so that the polysaccharide chain in this case has the following form: (the type of bond is indicated in brackets above the line representing the bonds): (1,3) glucuronic acid (1,4) glucose (1,3) glucuronic acid (1,4) glucose (1,3) etc.

replacing the hydrogen of the mineral acid (e.g. carrageen is an ester of sulfuric acid and the carbohydrate is, apparently a mixture of the sodium, potassium and calcium salts of the ester acid).

20. Each compact group of complex carbohydrates represents not one individual substance, but a mixture of related substances. In the majority of cases each of these mixtures consists of polymer homologs, composed of the same units (repeating the more or less complex units of one or several monosaccharide residues), but differing in the numbers of these units in the molecule. Thus, for example, starch amylose is a mixture of polymer homologs, composed of repeated glucose residues joined by α-1,4-glucosidic bonds but of different molecular weight. Complex branched-chain carbohydrates are also mixtures of polymer homologs. Thus, starch amylopectin is also a mixture of polymer homologs of different molecular weights. This does not exclude the possibility that irregularly branched chain polysaccharides, approximating to a compact group of polysaccharides, can differ also in their degree of branching.

In conclusion it must also be mentioned that the structural generalizations considered in this article are a consequence of general regularities in the structure of plant substances,[1] and are not isolated. Thus, the structural generalizations for monosaccharides in general relate to general and special limitations of the chemical composition of plants. Generalizations about the regular repetition of units in complex carbohydrates are evidence of a law governing the repetition of units in plant substances. The generalizations relative to the multiplicity of subdivisions of polysaccharides into separate close groups are evidence of a law governing the multiplicity of subdivisions of plant substances.

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[1] We note that generalizations about the structure of plant carbohydrates may be extended in general to animal carbohydrates, since in spite of considerable differences between the compositions of the complex carbohydrates in plants and animals, the structural plan of their molecules is similar.

ROLE OF AMINO ACIDS IN A SOLUTION WHICH REMOVES
SERICIN FROM RAW SILK

V. N. Krestinskaya and M. B. Aimukhamedova

In our previous paper [1], we reported experiments which established beyond doubt that solutions containing products of the hydrolysis of sericin as a rule almost completely removed sericin from raw silk.

In an investigation carried out somewhat earlier by one of us [2], it was established that the active substance in solutions capable of peptizing sericin and transferring it from fiber into solution, passes through parchment paper. From this it was concluded that this peptizer is either present in true solution in water, or is of such a high degree of dispersion that its particles are capable of penetrating parchment.

It would be more natural to suppose that the peptizing is done by amino acids, which are the final hydrolysis product of the protein molecule of sericin. It was supposed that these amino acids, being related to sericin, would be adsorbed by it, and since they are soluble in water, they could stabilize the sericin micelles. It was necessary to confirm this supposition. A number of considerations were required to establish the chemical nature of the stabilizer.

Above all, the fact of the existence of a stabilizer in protein solutions was of theoretical interest. It was important to elucidate what substance in these solutions can play the part of a stabilizer; apart from this it might be possible to follow its quantity in solution and to increase its concentration in cases where it is present in insufficient quantity, e.g., in baths for repeated use; it was also desired to go into the preparation of these solutions in more detail.

For confirming the assumption that the stabilizers of the sericin micelles are amino acids, a number of experiments were carried out by different methods but having one aim: to compare the activity of solutions containing amino acids.

EXPERIMENTAL

Investigation of dialyzation water. The first series of experiments were carried out with the object of studying the dialyzation water obtained in the process of preparing the solution. 8 g of broken-up cocoons were placed in a dialyzing vessel and 500 ml of distilled water were poured on them in it, another 500 ml was poured into the surrounding vessel. The relation between the quantity of silk and water was kept the same as in previous experiments. The water in the dialyzer was left unchanged for 5 days (time of preparation of solution).

We supposed that such an experimental arrangement would accelerate the hydrolysis of sericin, that a larger quantity of stabilizer would be formed and would pass through the membrane and that this would facilitate the preparation of more active dialyzation water. At the end of 5 days, the solution from the vessel and the dialyzation water were tested: their capacity for removing sericin from raw silk was checked and the nitrogen was determined by the Kjeldahl method;

in this way it was intended to obtain an indication of the quantity of amino acids present in the solution.

To determine the percent of sericin taken into solution, a weighed quantity of fiber was boiled in a small flask fitted with a reflux condenser; the boiling was carried on for 3 hours, after which the fiber was washed, dried at 105-110° and weighed. The modulus was 1/100. The results of the determination are set out in Table 1.

Table 1

Results of Investigation of Dialyzation Water

Solution No.		Solution	Sericin taken up (in %)	Total nitrogen in 50 ml solution	
				(mg)	(in relative %)
8	{	From dialyzer	20.07	0.7	100
		Dialyzation waters. . .	18.80	0.2	28.6
10	{	From dialyzer	23.80	1.74	100
		Dialyzation waters. . .	18.70	1.21	69.5
11	{	From dialyzer	22.17	0.83	100
		Dialyzation waters. . .	21.5	0.51	61.9

The results of the experiments set out in Table 1, confirm the observation made earlier, to which we referred above. All the dialyzation waters from the three solutions were active, since water under these conditions never takes up more than 15% (of sericin). Thus it was confirmed that the active substance in solution penetrates parchment paper. In all the experiments the solutions in the dialyzers were more active than the corresponding dialyzation waters, excepting No. 11, where the activity of both solutions was practically identical. As though in correspondence with this, the quantity of nitrogen found in the solution was always larger than in the dialyzation water. But no correlation could be established by comparing the results of different experiments.

Since the solutions from the dialyzer could always contain not only amino acids, but also sericin and polypeptides, and the dialyzation waters could contain polypeptides, it was decided to determine the amino acids directly by the copper method. The results of experiments, carried out with some solutions, are set out in Table 2.

The results obtained are extremely interesting; they demonstrate the existence of a correlation opposite to what we had supposed: the solutions which are better at taking up sericin (Nos. 18, 13, and 19) contain less amino acids in 50 ml (0.382, 0.336 and 0.370 mg N) than solutions having a lower activity (Nos. 14 and 22) containing 0.739 mg N in 50 ml.

It should, however, be noted that in the determination of the quantity of amino acids both in this series of experiments and also in others carried out at the same time, no control experiment was made. When the results of such experiments are allowed for, the quantity of amino acids in active solutions is lowered still further, frequently approaching zero.

Increase of the activity of solutions by concentration. A second series of experiments was carried out with solutions which were either very weakly active or were practically inactive. All these solutions were obtained by the usual methods at room temperature. It was supposed that their inactivity was due to

a low concentration of active substance. In order to raise the concentration, part of the solution was evaporated on a water bath to diminish the volume 2, 3, and 4 fold. Afterwards, the activity on raw silk fabric was tested by the usual method, both for the initial solution and for the concentrated one. In parallel the total nitrogen was determined in the solutions, after precipitating the sericin with alcohol, the sericin not being precipitated in the copper method; the amino acid nitrogen was also determined. Modulus 1/100. The results of the experiment are set out in Table 3 where the solutions obtained by concentration, are designated by priming the number applied to the initial solution.

Table 2

Dependence of the Activity of Solutions on Their Amino Acid Content

Solution No.	Method of preparing solution	Sericin taken up (in %)	Quantity of nitrogen in 50 ml solution (in mg)	
			Total	Amino acids
13	Dialyzate	24.3	—	0.336
14	Prepared by the usual method . .	18.7	—	0.739
18		24.6	—	0.382
19		21.2	0.700	0.370
22		13.3	0.931	0.739

Table 3

Dependence of the Activity of Solutions on Their Concentration

Solution No.	Degree of concentration	Sericin taken up (in %)	Quantity of nitrogen-containing substance (mg) in 50 ml solution, calc. as N			
			total	sericin	poly-pep-tide	amino acid
6	0	18.02	0.49	—	—	0
6'	3	23.64	0.84	—	—	0
7	0	17.1	1.05	—	—	0
7'	4	24.4	—	—	—	0
8	0	15.3	0.56	0.07	0.323	0.173
8'	3	23.9	0.98	0.35	0.63	0
9	0	14.5	0.52	0.45	0.07	0
9'	3	23.4	0.77	0.28	0.49	0
10	0	18.5	0.77	0.17	0.01	0.591
10'	2	19.4	0.98	0.42	0.46	0.099

The first thing that attracts attention in Table 3 is that in all the 5 cases concentrating the solution causes a rise of activity. Solution No. 10, concentrated 2-fold, is seen to have had its activity raised less than solutions concentrated 3-4 fold. Thus, the assumption that the weak activity of the solution was due to an insufficient concentration of active substance was confirmed by these experiments. In addition to this, it is clear from the table that amino acids are not the active substances: they are completely absent in Solutions Nos. 6, 7 and 9, and do not appear in the concentrated, fairly active Solutions 6', 7' and 9'; amino acids were found in Solutions 8 and 10 but after concentrating these

solutions (as a result of which their activity increased considerably), the amino acid content sank to zero (Solution 8'), or dropped considerably (Solution 10'), in the latter case the concentration was less — only 2-fold.

That the quantity of total nitrogen did not increase in proportion to the diminution in volume is to be explained by the fact that evaporation of the solution threw down a precipitate, which was filtered off before investigating the solution. The quantity of sericin diminished in some experiments and increased in others. Hence, there is no foundation for relating the change of activity of the solution to the quantity of sericin contained in it.

A further point to which attention must be directed is the increase in the quantity of polypeptide nitrogen on concentrating the solution. Thus, we obtain a first indication that the active substance in solution is a polypeptide.

Ageing of active solution on storage. It was observed that solutions of good activity aged on storage. This resulted in a loss of activity and a change of their external appearance: the solutions became transparent and precipitates appeared on the bottom of the containing vessels. The observations on solutions which were aged appear in Tables 4, 5 and 6. Solution No. 13 was studied immediately after preparation. After storing this solution more than 2 months, a flocculent deposit had appeared on the floor of the container. Half the solution was filtered off (13a), the deposit was dissolved by heating in the remaining part of the liquid (Solution 13b). The activity and the content of amino acid was determined for both solutions (Table 4).

Table 4

Change of Activity of Solution 13 and Amino Acid Content in It During Ageing

Solution No.	Date of Experiment	Character of solution	Age of solution (in days)	Sericin taken up (in %)	Quantity of amino acid nitrogen in 50 ml solution (mg)
13	9/8/1947	Freshly prepared	0	21.4	0.336
13a 13b	11/17/1947	Aged	70	15.8	16.899
		Aged, and precipitate redissolved	70	15.2	31.418

Table 5

Change of Activity of Solution 9' and of its Amino Acid Content During Ageing

Date of Experiment	Age of solution (in days)	Sericin taken up (in %)	Quantity of nitrogen-containing substance in 50 ml solution (in mg) calc. as N	
			total	amino acid
10/21/1948	0	20	—	0
12/4/1948	44	15	0.70	0.69

Table 6

Change of Activity of Solution 8' and of Its Amino Acid Content During Ageing

Date of Experiment	Age of solution (in days)	Sericin taken up (in %)	Quantity of nitrogen-containing substance in 50 ml solution (in mg) calculated as N			
			total	amino acid	sericin	polypeptide
9/20/1948	0	23.9	0.98	0.35	0.63	0
10/13/1948	23	24.9	0.63	0.21	0.43	0
12/3/1948	74	22.4	−	−	−	0

The activities of both solutions (13a and 13b) are practically identical; they are considerably lower than the activity of the freshly prepared solution; the quantity of amino acids had increased considerably. The large difference in the quantity of amino acids in solutions 13a and 13b indicates that the precipitate contained a large quantity of amino acids. At the same time it was evident that the presence of considerable quantities of amino acids in solutions did not affect their activity. Amino acids do not peptize sericin, but, evidently, do not prevent its peptization. It is true that the 15.2% of sericin taken up by Solution 13d is close to the quantity taken up by water from fabric.

Solution 9', the experimental data for which are given in Table 5, had an average activity, and contained no amino acids. After 44 days, its activity had sharply fallen; after this period amino acids were observed to have appeared, the quantity of nitrogen in which was practically equal to the total nitrogen of the solution. No peptizing action of these amino acids was observed.

Solution 8' was an interesting example of one having a higher activity (Table 6). This solution had a considerable activity and amino acids were completely absent from it. Tested after 23 days, it showed an increase of activity, amino acids again being absent. Even after 51 days the solution remained active, though the activity had somewhat diminished; amino acids were absent. After 23 days keeping, the quantity of polypeptide in the solution was lower than at the start, while the activity of the solution had increased. We do not find in this experiment such a simple relation between the activity of the solution and its polypeptide content, as was observed in experiments presented in Table 3, but all these experiments on ageing indicate that freshly prepared active solutions do not contain amino acids. Diminution of total nitrogen and formation of a precipitate go hand in hand.

Loss of activity of the solution on boiling. On boiling a solution, the same change should occur as a result of hydrolysis as occurs on keeping the solution, but all processes should be very much faster. Consequently, a lowering of the activity and an increase of the amino acid content should be expected on boiling a solution. The results of experiments are set forth in Tables 7 and 8.

The data of Table 7 confirmed our expectations; they showed that boiling a fairly active solution for 3 hours caused a loss of activity and increased its amino acids content; boiling the solution for 2 further periods of 3 hours did not induce any further change in it. It is probable that this solution was very poor in nitrogen-containing substances (exclusive of sericin), as a result of which all the nitrogen-containing substances were converted to amino acids in the first 3 hours.

Another experiment on the change induced by boiling was carried out with Solution 9'.

The data of Table 8 show that boiling this solution reduced its activity, but in contrast to Solution No. 19 (Table 7) No. 9' remained active and the quantity of amino acids was zero. Boiling for a further 6 hours reduced the activity of the solution further, but it still remained active and did not contain amino acids.

After 44 days the activity of the solution fell sharply, and a determination of amino acid and of total nitrogen in it showed that all the nitrogen in the solution was in the amino acids. This solution was

Table 7

Change of Activity of Solution No. 19, and of its Amino Acid Content on Boiling

Time of boiling (hours)	Sericin taken up (in %)	Quantity of amino acid nitrogen in 50 ml solution (mg)[1]
0	21.20	0.370
3	16.00	0.456
6	15.70	0.456
9	16.70	0.456

of interest in that the quantity of total nitrogen in it at 50 days had hardly changed, i.e., the amount of precipitate thrown down during the whole time was small. It is possible that its stability, like that of Solution 8', is bound up with its method of preparation: concentration on the water bath.

Table 8

Change of Activity of Solution No. 9' and of its Nitrogen-Containing Substances on Boiling

Date of experiment	Time of boiling (hours)	Sericin taken up (in %)	Quantity of nitrogen-containing substance in 50 ml solution (mg) calculated as N			
			total	sericin	polypeptide	amino acid
10/15/1948	0	23.4	0.77	0.28	0.49	0
10/20/1948	3	22.4	-	-	-	0
10/21/1948	9	20.0	-	-	-	0
12/4/1948	9[2]	15.1	0.70	-	-	0.69

Change of activity of the working solution in the process of preparation. As already noted in our first paper [1], solutions obtained under identical conditions differed sharply from one another in activity. It was decided to follow the change of activity and amino acid content in some solutions during their preparation (5 days). We treated, as usual, the broken-up cocoons with water (8 g cocoons in 1,000 ml water) and afterwards on each day withdrew a part of the solution for investigation.

The results obtained are set out in Table 9, from which it is seen that Solutions Nos. 1 and 3 showed each day a regular increase of activity, while the quantity of amino acids in them gradually fell to zero. Solution No. 2 behaved differently. On the second day, it attained a maximum activity and afterwards this fell gradually. The content of amino acids followed this change of activity: in Sample 1, having a minimum activity, we find the maximum content of amino acids; Sample 2 had a larger activity and the amino acid content in it was zero; in Samples 3, 4 and 5 the activity of the solution gradually fell and the amino acids content in it likewise gradually increased.

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[1] No control experiment.
[2] The solution was boiled for 9 hours but was stored afterwards for 44 days.

Table 9

Change of Activity of the Working Solution During Preparation

Solution No.	Date of commence-ment of preparation	Sericin taken up (in %) after (days)					Amino acid nitrogen in 50 ml solution (in mg) in tests				
		1	2	3	4	5	I	II	III	IV	V
1	1/6/1948	14.7	18.0	18.5	23.3	–	3.01	2.76	2.34	0	–
2	1/18/1948	12.9	18.9	16.7	16.6	16	0.62	0	0.10	0.25	0.32
3	1/28/1948	12.3	12.5	15.5	15.8	20	0.44	–	0.58	0.43	0

Thus, during the preparation of these solutions the same relation between the activity and the amino acids content was observed.

SUMMARY

1. The activity of the dialyzation water obtained from solutions containing products of hydrolysis of sericin has been demonstrated, and thus the molecular dispersity, or the very high degree of dispersion of the active substance has been confirmed.

2. The supposition that the active substance in solution is an amino acid was not confirmed, since the more active solutions contained smaller quantities of amino acids.

3. Concentration of the solution raised its activity, in parallel with which the quantity of polypeptide increased, but the content of amino acid sharply diminished or fell to zero.

4. On storing the solutions they aged, their activity and the quantity of polypeptide in them diminished, while the quantity of amino acids increased.

5. On boiling, the solutions likewise aged, lost activity and increased in amino acid content.

6. In the process of separation of solutions, an elevation of the activity of the solution was accompanied by a diminution in its amino acids content, while a fall of activity was accompanied by an increase in the quantity of amino acids.

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[1] See Consultants Bureau English translation, p. 711.

PROPERTIES OF COAGULATES OF PHENOL-FORMALDEHYDE RESINS PRECIPITATED

FROM AQUEOUS SOLUTIONS BY SALTS OF POLYVALENT METALS [1]

A. A. Berlin, D. G. Bernshtein and M. V. Sobolevsky

The addition of salts of polyvalent metals to a mixture of resin and fibers suspended in water, particularly the addition of aluminum sulfate, coagulates the resin and forms a difficultly soluble complex, which is deposited on the surface of the fiber. In the formation of a sheet and on further drying, the particles of resin form films partially or completely covering the fiber. The water-resistance of the sheet obtained depends on the type and quantity of the resin used, on the uniformity of its deposition, and on the completeness with which the fiber is enveloped.

Thus, it can be said that the properties of the sized fiber depend to a large degree on the properties of the coagulate adsorbed upon them.

Until recently, there was no experimental information in the literature about the properties of products precipitated by salts of polyvalent metals from aqueous solutions of phenol-formaldehyde resins. Our work was directed to the elucidation of the behavior of the coagulates mentioned above at higher temperatures and in solvents.

From the experimental data obtained, we worked out a method permitting the fairly accurate determination of the quantity of the coagulation products of water-soluble resins held up by the fibers.

EXPERIMENTAL

The main details of the method we used for the preparation of samples of resin coagulates were as follows.

The coagulates obtained by the precipitation of water-soluble phenol-formaldehyde resins of type "C - 1" were washed completely free from the precipitating electrolyte, dried at room temperature, after which their solubility in organic solvents was studied. The part of the coagulate insoluble in water was filtered off, dried to constant weight, and ashed. The difference between the weight of dry residue and ash was taken as the organic part of the dry residue, this being the resin which formed a chemical or association compound with the precipitating reagents. The soluble part of the coagulate was filtered from the precipitate, evaporated, and dried to constant weight, after which it was also ashed. The difference between the weight of dry residue and of ash corresponded to the organic part of the filtrate, or to that part of the resin which went into solution together with the precipitating salt.

The water-soluble phenol-formaldehyde resin, which we took for investigation, had the following characteristics:

Viscosity	14°E	Dry residue	41.94
Rate of polymerization (on the sheet)	15 secs.	Free phenol	8.65
Moisture	58.66%	Ash	7.90

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[1] Paper V of a series dealing with the chemistry and technology of high-molecular compounds.

TABLE 1

Softening Points and Rates of Polymerization of Phenolformaldehyde Resins
Precipitated from Solution

Method of precipitating coagulate		Softening point (in deg)	Rate of Polymerization at 140° (in sec)
Initial resin		75	15
Coagulate obtained by precipitating resin with	Sulfuric acid	110	13.9
	Phosphoric acid	115	22
	Potash alum	Did not soften	At 140° threads could not be drawn from the mass
	Ferrous sulfate	Did not soften	At 140° threads could not be drawn from the mass
	Technical alumina	Did not soften	At 140° threads could not be drawn from the mass

Table I gives information about the softening temperatures and rates of polymerization of films of the initial resins and coagulates, obtained by precipitating with different salts and acids.

The coagulates obtained by precipitating the resins with phosphoric and sulfuric acids softened at 75-115°. The rate of polymerization on a block at 140° was 15 sec. The coagulate obtained using phosphoric acid went over to stage " C " more slowly than those precipitated with sulfuric acid. None of the coagulates obtained by precipitation with sulfuric acid melted nor could threads be drawn from them. On heating, they behaved in the same way as resins, goingto stage " B ".

Comparison of Tables 1 and 2 shows that the properties of the coagulated resin formed depend on the precipitant used.

Resins dried in air may be dissolved once again in water. The coagulates, obtained by precipitating with different salts, are not soluble in water but are soluble in 1% caustic soda.

The coagulates obtained with phosphoric or sulfuric acids dissolved in alcohol, acetone, alcohol-benzene mixture and some other organic solvents, while the original resins and also the coagulates obtained by precipitation with salts either dissolved only partially in these solvents, or did not dissolve at all.

More complete solution was obtained by using acetic acid. In this case 98.83% of the whole weight of the resin was found in the filtrate (Table 2). 88.39% of it was organic substance, which in essence was soluble resin. The remaining, inorganic, part of the filtrate (9.44%) consisted in essence of sodium acetate. On boiling the coagulates obtained from potash alum or technical alumina with acetic acid, 90.99% went into the filtrate, of which 83.82% was organic in nature.

On the basis of the data adduced, the following ideas can be expressed about the mechanism of the process occurring in the precipitation and solution of the resins.

The phenol-formaldehyde resin, used for preparing the sized fiber materials, obtained in the presence of considerable quantities of alkali, in all probability contains a definite quantity of complex resin compound with the alkali metal,

we shall call henceforth the "resinolate" of the given resin. As a result of
the presence of such phenolate-like compounds, the resin is completely insoluble
in neutral organic solvents. The presence of resinolate of the univalent metal,
sodium, does not prevent the fusion of the resin, since in this case the exis-
tence of the trimeric structure is impossible. This suggestion is confirmed
by the fact that on precipitating the resin with acids, or on decomposing resin-
olates with acetic acid, the resin becomes soluble in neutral organic solvents.

The coagulates obtained by acting on solutions of resin "C-1" in aqueous
alkali with salts of polyvalent metals, are apparently mixtures of the resin-
olates of polyvalent metals. These resinolates should have a trimeric struc-
ture, since aluminum can bond intermolecularly with 3 phenolhydroxyls. The
presence of such aggregates in the resin should impair and, when their content
is large, should even completely nullify the ability of the coagulate to sof-
ten on heating.

The possibility of polycondensation and transition of the resins to the
"C" stage is not excluded since at a sufficiently high temperature intermolec-
ular condensation of the methylol groups with the hydrogens of the aromatic
nucleus can occur. The infusibility of the precipitates, obtained by using
salts of polyvalent metals, their incomplete solubility in neutral organic sol-
vents and the decomposition of the compounds obtained by weak organic and mineral
acids, all serve to confirm the supposition about the formation of trimeric
intermolecular resinolates. A study of the chemical nature of the coagulates
obtained and a more detailed investigation of the mechanism of formation of resin-
olates of polyvalent metals, will be the object of further investigation.

Method of determining the retention of resins in sheet plastic K-1. The
work carried out showed that caustic soda or acetic acid are the best solvents
for resins and coagulates. Control experiments performed to confirm the action
of alkali on cellulose fiber, present in the plastic, showed that the loss in
weight on boiling with 0.5% caustic soda for 4 hours was 12.65% on the fiber
taken; this indicates the inexpediency of extracting the polycondensate with
alkali.

No notable loss was observed when the fiber was treated with 70% acetic
acid. For determining the quantity of residual resin, test sheets were pre-
pared which were immersed in a laboratory extraction apparatus. The effluent
water was collected and the quantity of resin determined in it.

Table 3 gives data on the resin balance obtained in the sizing of fiber;
this data was found by extraction with acetic acid.

From this data it is seen that 84-87% of the quantity of resin supplied
is extracted from the sheets. 93.13% was extracted from Sheet No. 5. The
remaining part is not bonded to the fiber and is recovered in the process of
treating the material with washing water, in which it was discovered (Table 4).

On the basis of the work carried out, the following method of determining
resin in fiber material sized with resins, was worked out.

6-8 g of the material sized with resin, carefully cut up, is placed in a
thimble of filter paper. The thimble is placed in a Soxhlet apparatus to which
70% acetic acid is added (taking care that the quantity is insufficient to
produce siphoning), and is left to stand for 8-12 hours, after which the neces-
sary quantity of acetic acid is placed in the extraction flask and the extrac-
tion is carried on for 6 hours.

The resin content is determined either on the dry extracted substance, or

TABLE 2

Solubility of Resins and Their Coagulates in Organic Solvents

Name of solvent	Solubility of initial resin						Solubility of coagulate from sulfuric acid					
	Precipitate			Filtrate			Precipitate			Filtrate		
	Organic substance	Inorganic substance	Total	Organic substance	Inorganic substance	Total	Organic substance	Inorganic substance	Total	Organic substance	Inorganic substance	Total
Alcohol	23.40	5.05	28.45	67.32	4.38	71.70	0.01	0.11	0.12	99.34	1.17	100.51
Acetone	28.86	6.80	35.66	62.03	2.32	64.35	0.07	0.06	0.13	99.71	1.18	100.89
Alcohol-benzene	29.17	5.92	35.73	61.34	3.22	64.97	0.10	0.48	0.58	100.0	0.72	100.7
Acetic acid	1.64	0.43	2.17	88.39	9.44	98.83	0.10	0.48	0.58	100.0	0.72	100.70

Table 3
Acetic Acid Extraction of Sheets Sized with Resin

Sheet No.	Precipitant	Weight of the whole sheet (in g)	Quantity			Quantity of resin relative to fiber (in %)	Quantity of extracted resin (in %)	Ratio of extracted to supplied resin (in %)
			of fiber	of resin	of precipitant			
1	Alumina	10.7596	6.0076	2.0080	1.7440	27.8	23.42	84.25
2	Alumina	18.7880	14.260	3.5770	0.9510	19.04	16.57	87.02
3	Alumina	9.8669	7.130	1.7859	0.954	32.1	19.22	86.97
4	Sulfuric acid	8.9197	7.1300	1.7894	--	25.09	21.27	84.77
5	Alumina	9.8642	7.1300	1.7882	0.951	18.7	16.94	93.18

Table 4

Balance for a Phenol-Formaldehyde Resin, Extracted with Acetic Acid from Sheets

Sheet No.	Quantity of resin taken (in %)	Quantity of resin extracted from the sheet (in %)	Quantity of resin found in the wash waters (in %)	Total quantity of resin extracted from the sheets and found in the wash waters
3	25.09	21.27	3.58	24.85
4	22.10	19.22	2.38	21.60
5	16.07	16.94	1.27	18.21

from the loss of weight of the weighed quantity of material taken for analysis. In the latter case, before drying the precipitate to constant weight, it is washed with distilled water to remove acetic acid adsorbed on the fibers. The moisture content in the material as taken for analysis is allowed for in calculating the resin content.

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Table 2 (Continued)

| Solubility of coagulate from potash alum | | | | | | Solubility of coagulate from technical alumina | | | | | |
| Precipitate | | | Filtrate | | | Precipitate | | | Filtrate | | |
Organic substance	Inorganic substance	Total	Organic substance	Inorganic substance	Total	Organic substance	Inorganic substance	Total	Organic substance	Inorganic substance	Total
16.78	3.01	18.79	79.63	0.77	80.40	33.53	9.38	42.91	65.38	0.20	65.38
7.40	3.84	11.24	87.94	0.82	88.76	41.81	7.59	49.40	47.59	1.68	49.37
11.61	3.43	15.04	84.13	0.77	85.90	37.17	8.93	46.16	51.92	0.39	52.31
5.53	0.40	5.93	90.99	4.01	95.0	7.21	0.97	8.28	83.82	8.80	91.62

SUMMARY

1. The possibility of obtaining coagulates of resins with different salts and acids has been demonstrated.

2. The deposits obtained may be characterized by their fusibility and rate of polymerization at different temperatures.

3. The formation of "resinolates" in the process of precipitating resin with polyvalent metals, is discussed, these "resinolates" being trimeric molecules.

4. The best solvent for the coagulates, obtained in sizing organic fibers with phenol formaldehyde resins, is 70% acetic acid.

5. A method for extracting resins from fibrous material sized with phenol formaldehyde has been worked out.

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EFFECT OF CERTAIN METAL OXIDES ON THE STABILITY OF PERVINYLCHLORIDE RESINS AT ELEVATED TEMPERATURES [1)

I. I. Denker and A. A. Berlin

A number of oxides of polyvalent metals, for example, ZnO, Fe_2O_3, TiO_2, Cr_2O_3, find wide application as pigments for inclusion in different film-forming materials and, in particular, in polyvinylchloride and pervinylchloride.

The presence of these pigments may have a considerable influence on the stability of the films at high temperatures, and in particular on the rate at which hydrogen chloride is liberated from them. A systematic study of this matter is of considerable theoretical interest.

EXPERIMENTAL

We investigated the effect of certain pigments on pervinylchloride resins. Chemically pure metal oxides were used, which were carefully stirred up with butyl alcohol and were introduced as a paste into a solution of the resin. The films obtained from the solution were subjected to the usual physico-mechanical tests, and, apart from this, the rate of fission of hydrogen chloride at 130° from them and the change in their solubilities were measured.

The effect, at high temperatures, of the quantity of pigments on the rate of separation of hydrogen chloride and the transition of pervinylchloride to the insoluble state was determined only with ZnO as pigment; this material had a marked effect on the separation of hydrogen chloride and the formation of an insoluble polymer. The determination of the quantity of hydrogen chloride separated from the films, which became insoluble, is extremely difficult, because the films swelled very little even in hot water; hence, for complete extraction of the $ZnCl_2$ from the films, a special method was required, as follows.

A film heated to 130° was carefully cut up. A weight of the sub-divided film (about 2 g) was put in a flask with a reflux condenser, to which 100 ml of a mixture of acetone and water was added and then the flask was heated for 2 hours at 55-60°. The resin, treated with aqueous acetone, was transferred to a filter and washed with warm distilled water, until all traces of chlorine had disappeared.

In the filtrate the quantity of chlorine was determined by titration with 0.01 N $AgNO_3$; the film, washed out, was dried in a vacuum oven at 40° to constant weight and then utilized for the determination of solubility.

The experimental data obtained are set forth in Table 1.

As we see, the presence of even small quantities of ZnO considerably accelerates the separation of hydrogen chloride on heating and the transition of the 3 double bonds in pervinylchloride to the insoluble state. It is possible that both these processes are catalyzed by zinc chloride, produced by interaction of the ZnO with the HCl formed.

[1) Communication VI from a series dealing with the chemistry and technology of high molecular compounds

TABLE 1

Effect of ZnO Content in Pervinylchloride Films on the Quantity of HCl Separated and on Their Solubility

Pigment	Quantity of pigment (in % on wt. of resin)	Quantity of HCl separated (in % on weight of resin)			Solubility of resin in chlorobenzene after heating (in %)		
		Time (in hours)					
		1	2	3	1	2	3
Without pigment	0	0.04	0.18	0.30	100	80	63.2
Zinc Oxide	0.5	0.10	0.41	0.44	100	0	0
	1.0	0.23	0.37	0.40	100	0	0
	3.0	0.20	0.803	1.09	100	0	0
	6.0	0.23	1.60	2.95	100	0	0
	10.0	1.58	4.67	5.98	Swelled	0	0

Effect of the chemical nature of pigments on the separation of hydrogen chloride. For elucidating the effect of the chemical nature of the metal oxides on the rate of separation of HCl, films containing 10% of various metal oxides on the weight of the resin were tested. The results obtained are set forth in Table 2, from which the following conclusions may be drawn.

1) The quantity of HCl separated depends on the chemical nature of the pigments and on the time of heating.

2) There is the most intense separation of HCl in films containing zinc oxide and ferric oxides. Chromium oxide is considerably less effective. Aluminum powder not only does not increase the separation of HCl, but somewhat stabilizes the pervinylchloride.

TABLE 2

Effect of Chemical Nature of Pigment on the Thermal Stability of Pervinylchloride at 130°

Pigment	Quantity of pigment (% on wt. of resin)	Quantity of HCl (in % on weight of resin)					Solubility of resin in chlorobenzene after heating (in %)				
		Time (in hours)									
		1	2	3	5	8	1	2	3	5	8
Film without pigment	0	0.04	0.18	0.303	---	0.65	100	80.0	63.2	---	0
ZnO . . .	10	1.58	4.67	5.98	6.62	11.41	Considerable swelling	0	0	0	0
Fe_2O_3 . .	10	0.75	0.76	1.82	4.88	---	100	Considerable swelling	0	0	0
Cr_2O_3 . .	10	0.07	0.21	0.22	0.751	1.65	100	100	Considerable swelling	0	0
Al . . .	10	0.03	0.04	0.21	---	0.78	100	100	100	100	100

Films containing zinc and ferric oxides undergo a sharp change in their color when heated. Films pigmented with zinc oxide, which are white, and with ferric oxide, which are red, become completely black after 4-5 hours heating at 130°. Films pigmented with aluminum powder only slightly darkened. Such changes in the solubility and physico-mechanical properties of films in the presence of pigment only occurred at raised temperatures. No change in the solubility of the films was produced by heating them for the same time at 80°.

Physico-mechanical properties of pigmented films. The interaction of macromolecules of pervinylchloride, leading to the formation of trimeric structures on heating, is considerably faster in pigmented pervinylchloride films than in the unpigmented ones. Apparently, the salts formed catalyzed on the formation of HCl and the trimeric polymerization of the macromolecules of pervinylchloride containing free double bonds; hence under identical conditions, the change in physico-mechanical properties of pigmented films on heating is more extensive (Table 3).

TABLE 3

Effect of Heating on the Change of the Physico-Mechanical Properties of Pigmented Pervinylchloride Films at 130°

Pigment	Quantity of pigment (% on wt. of resin)	Strength (in kg/mm²) Time of heating (in hours)					Extension (in %)					No. of double bonds				
		1	2	3	5	8	1	2	3	5	8	1	2	3	5	8
Film without pigment	0	3.8	4.2	4.5	4.7	5.6	5.4	4.2	3.0	3.0	3.4	173.0	61.2	39.2	28.0	10.6
ZnO	10	4.22	5.4	5.48	Film tore on clamping		4.0	2.5	2.0	---	---	7.2	5.6	0	0	0
Fe₂O₃	10	2.04	Film tore on clamping				4.0	---	---	---	---	18.8	10.0	6	0	0
Cr₂O₃	10	3.5	3.6	3.94	4.38	4.88	3.5	3.0	2.0	2.0	1.5	51.8	40	33	19.6	7
Al	10	1.36	2.15	2.4	2.4	2.8	3.5	1.2	1.0	1.0	1.0	---	---	---	---	---

The experimental data presented in Table 3 confirm this conclusion.

After 3-5 hours heating, the films pigmented with zinc and ferric oxides became somewhat brittle so that their physico-mechanical properties could not be determined. The films tore on clamping in the dynamometer.

The effect of heating on the change of the structure of pigmented films may be illustrated by the testing of films for elasticity, by Ericsson's method. The data obtained are in Table 4.

From these data it follows that the stability of pervinylchloride films depends not only on the time and temperature of heating, but also on the nature and quantity of the metal oxides present in them.

TABLE 4

The Effect of Heating on the Elasticity of Films (Ericsson) at 130°

Film		Duration of heating (in hours)			
		0	1	2	3
Films with 10%	ZnO	4.23	0	0	0
	Fe_2O_3	5.45	3.2	0	0
	Cr_2O_3	5.67	5.50	5.40	4.33
	Al	1.25	0.7	0.6	0.6

justified for polymers having a linear structure. In those cases where trimeric structures can be formed on raising the temperature, as happens, for example, on heating pervinylchloride, not only does a rise of temperature not increase the adhesion of the films to metals, but in fact, sharply decreases it.

The corresponding experimental data are presented in Table 5.

TABLE 5

Adhesion of Films to Metals, Determined by Ericsson's Method

Film		Temperature of heating (in °C)			
		80	130		
		Time of heating (hrs)			
		3	1	2	3
Films with 10%	ZnO	2.75	0	0	0
	Fe_2O_3	3.2	2.95	0	0
	Cr_2O_3	3.2	3.00	3.15	3.2
	Al	2.3	2.7	2.0	2.42

Effect of change of structure of films on their adhesion. In a number of theoretical and practical studies of the effects of fundamental factors on the change of the adhesion of polymerized resins to metals, indications may be found that the adhesion increases with the temperature of the dry coating. This is confirmed by our study of the effect of different factors on the adhesion of pervinylchloride to metals, but it should be mentioned that this assertion is only justified for polymers having a linear structure.

As can be seen from the data of Table 5, after 3 hours heating at 80°, the adhesion of chlorinated pervinylchloride to metals is fairly high. At this temperature HCl does not separate and the formation of the trimeric structures does not take place. (Solubility of the resin quite unchanged). When samples of metals, covered with pervinylchloride containing ZnO and Fe_2O_3 were heated to 130°, a transition of the polymer to the insoluble state and a sharp reduction of the adhesion were observed. The introduction of aluminum powder into the resin is practically without effect on the solubility or on the adhesion of the covering to the metal surface. Apparently, the removal of HCl, formation of insoluble trimeric polymers, and lowering of the adhesion of the covering, occur most strongly in the presence of basic pigments.

SUMMARY

1. It has been shown that basic oxides (ZnO, Fe_2O_3) accelerate the removal of HCl and the formation of insoluble polymers, while aluminum powder has practically no effect on this process.

2. It has been established that the formation of insoluble polymers on thermal treatment lowers the bend strength of the film and the adhesion of pervinylchloride coating to metals.

BRIEF COMMUNICATIONS

CALCINATION OF ULTRAMARINE CHARGES

A. N. Agte, P. I. Libina, A. D. Miller and A. P. Musakin

Leningrad Lensoviet Institute of Technology

Usually, the roasting of ultramarine charges is carried out in crucible or muffle furnaces. However, this suffers from a number of defects: 1) the process of ignition is too long; 2) the furnaces work periodically; 3) the regulation of the gas atmosphere in the furnaces is incomplete (effected by changing the thickness of the layer of fuel, cementing up the furnace openings with clay, etc.), which results in the formation of different forms of waste material; 4) the taking of samples for checking the ignition is practically impossible; 5) charging and discharging the furnace is laborious and detrimental; and 6) fireclay crucibles of uniform porosity are required.

Improvement of the technology of calcination is difficult because the formation of ultramarine is complex and has been little studied. The quantity of work which has been devoted to the study of the effect of different factors in the roasting of ultramarine charges is not great. This is explained by the difficulties involved in devising experiments. Up to the present, experiments have been carried out under production conditions in which the multiplicity of the simultaneously acting factors prevents the determination of the effect of separate factors. Calcination has scarcely been studied under laboratory conditions, since it has been assumed that it is impossible to create production conditions in laboratory furnaces; as a result, the ultramarine obtained in the usual laboratory crucible or muffle furnaces is of poor quality.

The patent literature on ultramarine is poor; in the main it does not indicate the conditions for the formation of ultramarine in calcination, but deals with the questions of the mechanization of existing methods of calcination, the replacement of crucible furnaces by those of different construction: retorts, tunnel and rotating furnaces [1-3]. What is evident from patents is the very general aim of the authors to replace batch methods of calcining by continuous methods, but in view of the absence of experimental data, many points in these patents are not clear.

The object of our work has been to seek such a method of calcining charges as would permit the shortcomings mentioned above to be eliminated to a considerable extent. For this purpose, it was necessary above all to find a method of laboratory preparation of ultramarine, enabling the effect of different factors of ultramarine formation to be studied in the process of calcination and at the same time to lay the basis for a new method of calcination under production conditions.

The formation of ultramarine during calcination, as is known, involves two stages.

In the first stage up to 500°, as a result of reaction between soda and sulfur, an alkali polysulfide is formed which, on further elevation of the temperature to 750°, interacts with the kaolin with the formation of green ultramarine. During this first period, there should be a reducing atmosphere in the furnace and the charge must be protected from the action of atmospheric oxygen.

Afterwards, in the second period of calcination, with gradual cooling of the furnace, the green ultramarine is slowly oxidized by the oxygen of the air to the blue variety. In this period the access of air to the furnace should be carefully controlled.

In contemporary furnaces it is practically impossible to create the required gas atmosphere during this or that period of the calcination. Hence, in working out a new method, the aim was to carry out the calcination in a furnace which would permit isolation of the charge from air during the reducing period and control of the access of the air during the oxidizing period.

EXPERIMENTAL

For calcining the charges, a tubular electrical furnace (Fig. 1) was used.

The charge was placed inside the porcelain tube. The tube communicated with the air through the clip 7, the glass tap 11 and the liquid seal 10. Air was supplied through a blower.

The temperature in the furnace was measured with a thermocouple. The junction was located outside the tube around the heating spiral; the relation between the temperature at this point and the temperature at the center of the furnace had been previously established. The temperature in the furnace was held constant to within $\pm 7°$ by a thermoregulator. The rate of passage of air was measured with a flowmeter.
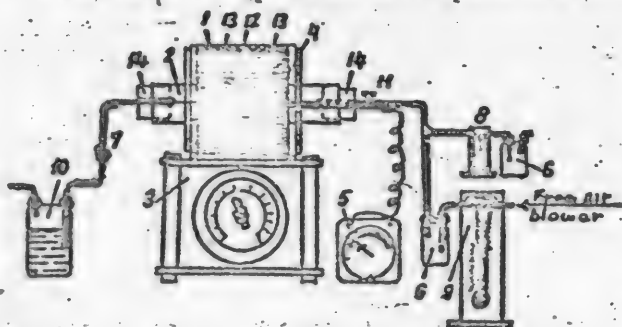
Fig. 1. Layout of laboratory apparatus for calcining ultramarine charges.

1) Tubular electrical furnace with thermoregulator; 2) porcelain tube (length 70 cm, internal 3 cm or, for another furnace 7 cm; 3) transformer; 4) thermocouple; 5) galvanometer; 6) catch pot; 7) clip; 8) manometer; 9) flowmeter; 10) liquid seal; 11) glass stopcock; 12) charge; 13) asbestos plug; 14) rubber bung.

The quality of the calcination product was determined visually by comparing it with different industrial samples. For a number of samples, the color and color intensity were determined in the laboratory of the "Republic" plant. Some of the samples were examined analytically.

In all cases, the usual ultramarine charge, as used at the above plant, was adhered to; it had the following composition (in %): Sulfur 30, soda 30, kaolin 30, infusorial earth 4, sand 6.

The conditions of calcination required for obtaining green ultramarine of good quality were established by a series of experiments, and afterwards the calcination conditions with access of air, resulting in the oxidation of green ultramarine to blue, in quality not inferior to the best plant samples, were then established.

As a result of these experiments, the running conditions set forth below were established; these conditions were maintained in all later investigations (Table 1 and Fig. 2).

Different oxidation temperatures were selected for different experiments (Fig. 2). The air rate for oxidation was usually 0.12 liter/min.

Table 1

Running Conditions

Temperature (in °C)		Time (hours)	Air feed
Rising	up to 300	1.5	None
	from 300 to 450	2.0	
	from 450 to 500	0.5	
	from 500 to 730	1.5	
Maintained at 730-750		6.0	
Falling to temperature of oxidation		1.0	
Maintained at oxidation temperature		3.0-6.0	Controlled air feed
Total		16-19	

Fig. 2. Temperature-time plot for calcination of ultramarine charges in a gas-tight tube.
A — Temperature (in °C); B — Time (in hours).

Effect of different factors on the quality of the products

While maintaining the temperature regime indicated above, the effect on the quality of ultramarine obtained of changing the oxidation temperatures was observed. The results of these experiments are presented in Table 2.

Table 2

Quality of Calcination Products at Different Oxidation Temperatures

Temperature (°C)	Time of oxidation (in hours)	
	3	6
630-650	Satisfactory (product whitish)	Unsatisfactory (product whitish)
580-600	Satisfactory	—
530-550	Good	—
400-420	Satisfactory	Very good
330-350	Satisfactory (product greenish)	Good
260-280	—	Good
200-220	—	Unsatisfactory (product greenish)

From the experimental data (Table 2), it is seen that ultramarine of satisfactory quality may be obtained both at high and low oxidation temperatures. A better product is obtained at the lower temperatures; it is more uniform, but the oxidation is slower.

The products obtained were analyzed at the plant mentioned. The intensity of the coloring of the oxidation products, according to data obtained in the plant laboratory, was about 130-150; the salt content was around 27-29%.

It should be mentioned that the data in the literature concerning the enhanced stability of the green ultramarine to oxidation at high temperatures was refuted by our experiments. The higher the temperature, the more rapid the oxidation and possibly, even the peroxidation, of the product.

The results of investigating the effect of time of oxidation on the quality of the calcination products are set forth in Table 3 (calcination conditions indicated in Table 1).

Table 3

Quality of Calcination Products at Different Temperatures and Times of Oxidation

Time of oxidation (hours)	Temperature of oxidation (in °C)		
	330-350	400-420	630-650
1.5	—	—	Satisfactory (product whitish green)[1]
3	Satisfactory (product greenish)[1]	Satisfactory[1]	Satisfactory (product whitish)[1]
6	Good[1]	Good	Unsatisfactory (product white)
9	—	Good	—
14	—	Very good (violet tinge)	—
19	—	Ditto	—
25	—	ʺ	—

From the data presented in Table 3 it is evident that, at an oxidation temperature of about 400°, the time interval over which satisfactory and good products of calcination are obtained is wider than at 630-650°. At 400-420°, good ultramarine is obtained after 6 hours; on extending the oxidation time the ultramarine quality was not lowered. At 630-650°, a satisfactory product was obtained after 3 hours; on extending this time the quality of the product diminished sharply.

In experiments to study the effect of the air rate under the conditions specified in Table 1, oxidation was carried on at different air rates; air was passed through the furnace for 6 hours at 400-420°.

This series of experiments was also carried out in a tube of large diameter (7 cm). In this tube, oxidation, without mixing, took somewhat longer (up to 10 hours).

As a result of these experiments it was established that the best ultramarine was obtained, in wide and small tubes, at air rates of 0.12-0.20 liters/min. The required air rate depends on the temperature and time of oxidation, the diameter of the tube, the mixing of the calcined charge and on other factors.

Under these calcination conditions, oxidation was extended for 6 hours at 400-420°. It was established that the period of pre-treatment at 730-750° (before oxidation) of 6 hours is a minimum one for obtaining good ultramarine (with 6-9 hours pre-treatment very good ultramarine was obtained, and at 0-3 hours unsatisfactory products).

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[1] Product contained small inclusions.

In experiments to find out the effect of the composition of the oxidizing gases, the oxidation of green ultramarine to blue was carried out with a mixture of air and carbon dioxide. A gas mixture containing 90% CO_2 and 10% air scarcely oxidized green ultramarine even at 800° for 6 hours at 0.15–0.20 liters/min. Oxidation with a mixture of equal volumes of CO_2 and air (each being fed at 0.35 liters/min) was considerably slower than oxidation with pure air (at the same rate 0.35 liters/min).

Thus, the possibility of peroxidation of ultramarine by such a mixture is reduced, a result which can be utilized, for example, in oxidation at higher temperatures.

After this, experiments were made to study the effect of the degree of filling of the tube and the stirring of the charge. The experiments were performed in the 7 cm diameter furnace. Calcination was made by two methods.

1. In both stages of calcination, the working space of the tube was not completely filled with charge: In the first period, the tube was not moved; in the second, the oxidation period, it was slowly turned around its axis.

2. In the first stage of calcination, the working space was completely filled with charge. Then in the second stage, the asbestos plugs were removed, and the charge was oxidized with stirring caused by slow rotation of the tube. This series of experiments was aimed at eliminating the volatilization of sulfur from the charge into the empty space in the tube, which was possible in the first series of experiments. The results of these experiments are presented in Table 4.

Table 4

Quality of Calcination Product as a Function of the Degree of Filling of the Tube and the Stirring of the Charge

Degree of filling (in %)		Time of oxidation (hours)	Stirring	Quality of products
in 1st stage	in 2nd stage			
100	100	10	Without stirring	Good
100	20	1.5	With stirring	Very good
100	80	3	Without stirring	Very good
100	80	3	With stirring	Very good
75	75	6	With stirring	Very good
50	50	3	With stirring	Satisfactory
25	25	3	With stirring	Unsatisfactory

The experiments showed the following:

1) During the first period of calcination (in which green ultramarine is obtained), stirring is not required, green ultramarine is best obtained with complete filling of the working space of the tube;

2) Good blue ultramarine may be obtained by oxidizing the green ultramarine in thin layers; the time of oxidation in this is considerably less; the temperature of oxidation may be 400°;

3) If both stages are carried out at identical degrees of filling of the tube, then this should not be less than 50%.

At very small degrees of filling of the tube, low-sulfur green ultramarine is obtained, and low quality blue material is obtained from it.

SUMMARY

1. The first stage of calcination of the charge to green ultramarine should be carried out without access of air, for example, in a hermetically closed muffle (drum).

2. The second stage of calcination — oxidation of green ultramarine to blue — should be carried out at a controlled air rate (or CO_2/air mixture rate); the temperature of the oxidation may be different (650-400°); oxidation can be more easily controlled at lower temperatures.

3. The first stage of oxidation should be carried out in a furnace with the working space completely filled with charge (or with not less than 75% filling); the second stage should be carried out with the charge stirred and, consequently, with an incomplete filling of the working space by the charge.

4. Since, in the conditions of calcination, both stages differ considerably, it is more convenient to carry them out in different furnaces. It is possible, however, to carry out the calcination at identical degrees of filling of the furnace by the charge so long as this degree is not too small (not less than 50%).

5. The time of calcination can be considerably shortened, by comparison with existing schedules, by controlling both periods.

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USE OF ELECTROMAGNETIC TRANSMISSION IN APPARATUS WORKING UNDER PRESSURE

B. E. Vishnevsky and N. M. Reinov

In contemporary chemical industry, various forms of apparatus for the mixing and displacement of volatile and corrosive liquids are widely used. Such apparatus works at high temperatures, and at pressures approaching hundreds of atmospheres.

As is known, to get a sufficient rate of reaction in the diffusional region, it is necessary to stir very strongly so as to increase the area of interface between the reacting substances. Such stirring is possible only with very high propeller rates or with blade mixers. The combination of a high shaft speed and considerable pressure on the gland, presents an almost insoluble problem. It is accepted that about 15 ml of liquid per minute should be permitted to leak through these glands [1].

The leakage leads to a loss of valuable raw material, impairs the conditions of work and not infrequently acts as a source of poisoning and fire.

The use of short-circuited asynchronous motors in which the rotor turns inside the apparatus, and is separated from the stator by a thin-walled screening bush, can solve the problem of constructing glandless apparatus.
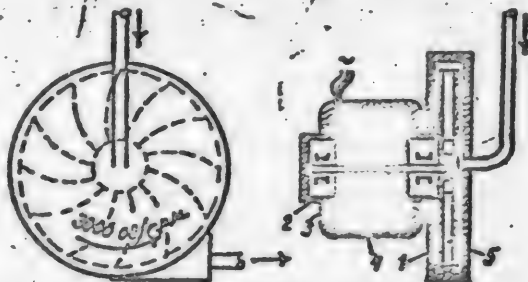

Fig. 1. Scheme for construction of the pump of a mechanical
gas analyzer.
1 — Housing; 2 — Rotor bushing; 3 — Rotor; 4 — Stator; 5 — Impeller.

For diminishing the power loss of the electric motor, the screen should be constructed of a material with a magnetic permeability of unity and a high specific resistance.

Some centrifugal glandless pumps, designed for working under a pressure of 10 atm. have been made and tested in the Leningrad Physico-Technical Institute.

As indicated in Fig. 1, the pump consists of a housing 1, inside which the impeller 5 rotates on the axis of the rotor 3. The screening sleeve 2 is firmly fixed to the housing of the pump. The stator of the electric motor 4, fits over the sleeve.

Such pumps proved extremely convenient in operation, since they require practically no servicing. They operate under a load of more than 300 atm. without any sort of maintenance.

The development and manufacture of the original "mechanical gas analyzers" was made on the basis of such a pump. In these pieces of equipment, the static head on the pump was measured by a sensitive Krel differential manometer. The apparatus determines gas density continuously and automatically. For the analysis of methane/hydrogen and nitrogen/hydrogen mixtures, the analytic error does not exceed 2% and when necessary may be lowered by raising the impeller rate. Such a pump may be used for the circulation of hot smoke-laden gases under pressure, for example, in the regeneration of catalysts.

Centrifugal glandless pumps may find wide application for the circulation of acids, volatile and poisonous liquids and also for the compression of gases.

In chemical industry, reactors and autoclaves may be introduced, equipped with effective and rapid mixers. Rotary rectification columns should be widely employed, having unusually large outputs and high efficiencies [2]. The use of a glandless construction permits the fabrication of columns rotating at 12,000 rpm and above, for working under any pressure, including low vacuum.

In Fig. 2 are set out the operating characteristics of two models of enclosed pumps, motor driven.

From the figures it is seen that the introduction of a screen with a magnetic clearance leads to some lowering of the power and coefficient of useful work of the motor. Increasing the clearance from 2.4 mm in the first model to 3.2 mm in the second, at large motor loading (S – 40%) reduces the useful mechanical power from 200 to 145 W.

At large loadings of the motor the coefficient of useful work is around 30%.[1]

The loss in the screen is relatively small. The main loss is conditioned by the increased magnetization current, caused by the increase of the magnetic clearance.
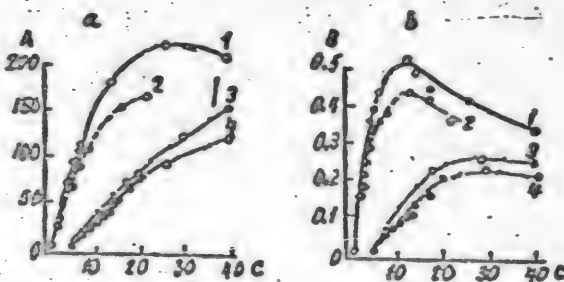

Fig. 2. Operating characteristics of two model sealed pumps.[2]
A – P (in W); B – K; C – Motor load (in %).
1 – model without screen; 2 – model No. 1 with screen; 3 – model No. 2 without screen; 4 – model No. 2 with screen; a – useful mechanical power of the motor (in W). b – coefficient of useful mechanical work of the motor.

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[1] The coefficient of useful work increases with increasing power of the motor and for 2.2 kW is 75%.
[2] The curves were taken in the laboratory of high frequency electrometry of the USSR Academy of Sciences, with the scientific collaboration of N. P. Glukhanov.

Thanks to the high speed of the pump and the absence of a seal the overall coefficient of useful work of the assembly is somewhat higher than when using gland transmission. The main superiority of electromagnetic transmission is the simplicity of servicing and the complete elimination of leaks of the gases and liquids being pumped.

The use of electromagnetic transmission makes it possible to create a new type of chemical apparatus for working under pressure.

LITERATURE CITED

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G. V. Kukolev: Chemistry of Silica and Physical Chemistry of Silicates.

State Publishing House for Literature on Building Materials.
Moscow. 1951. 616 pages., Edition of 3000 copies. Prof. G. V. Kukolev's
book, "Chemistry of Silica and Physical Chemistry   of   Silicates" has been
produced by the Ministry of Higher Education of the USSR as a text book for
Universities specializing in the "Technology of Silicates". At the conference
on methods of the chemical-technological Universities held in Leningrad in 1949
the educational program for the course "Chemistry of Silica and Physical
Chemistry of Silicates" was subjected to fundamental examination and broadening.
The necessity for this review was dictated by the present need to raise the
level of instruction in special subjects of our cadres of engineer-technicians,
working in the field of production of different constructional materials —
cement, constructional ceramics, refractories, glass, etc.

The high technical level of the industry of the USSR, its vigorous growth,
and the creation of new branches of production, require that our engineers
should have a deep knowledge of special subjects, as one of the extremely
important prerequisites for the development of industry and the improvement
of technology on a scientific basis. In essence the new program for the course
mentioned is a reconstruction of the theoretical side of specialist education
in the light of the current tasks facing industry.

Prof. Kukolev's book is a textbook written in the light of the requirements
of the new program, and hence including under one cover an exposition of the
chemical and physico-chemical behavior not only of silicates themselves, but
also of numerous other compounds, with which all branches of production bound
up with the silicate industry, are concerned. Among such compounds, carbonates
in particular should be mentioned, and also the oxides and hydroxides of the
alkaline earths, alumina and its hydrates, calcium aluminates, spinels, etc.

The book gives a fairly clear exposition of the current position of
silicate science. It demonstrates the enormous role of our own scientists in
the development of this science — scientists of both the older and younger
generations. The book shows that there is not a single subject, among a wide
enumeration of problems and individual topics covering the chemistry and
physical chemistry of silicates, which have not been worked on with success in
the USSR.

In his presentation of the material, the author aims not only to give the
necessary introduction to the discipline, but also set forth a knowledge of the
science of silicates and of other compounds in the silicate industry for the
solution of practical questions, and also to give instruction in the utilization
of the discipline for the solution both of practical and theoretical questions.
In large measure this relates to very large and complex divisions of the subject,
— study of phase equilibria and its numerous applications. The exposition of
many questions relating to the colloid chemistry of silicates is also important
for technology.

In the presentation of each physico-chemical system there is given, in a
definite order, the necessary complex introduction to the system and the properties

of its compounds, namely: 1) description of the phase diagram, its characteristic peculiarities and its practical significance; 2) the properties of the phases of the system; a) composition of the crystalline phases and their laboratory synthesis; b) natural minerals, their distribution and origin, hydrated minerals; c) the structure of the crystal lattices; d) crystalline systems, crystallo-optical properties, specific gravity, hardness, and other physical properties; e) various chemical properties of the solid phases; f) their colloid-chemical properties; g) the solid phase reactions which are of importance for the given system; and 3) the forms of technical utilization of its compounds which are of importance for the system.

The author gives a general theoretical introduction in the chapters on: study of phase equilibria, the solid state, the colloid state of silicates, the thermochemistry of silicates, the liquid state, the glassy state, and the electrochemistry of silicates and of some other dielectrics.

In a separate chapter there is an introduction to silicon compounds which are not directly related to silicates, in particular organosilicon compounds.

The book is not free from defects and incompleteness. Thus, the author ought to have carried through to the end the principle of the exposition of material for each system, extending it to the viscosity, surface tension of glasses and melts, the chemical stability, density, electrical conductivity, optical properties of glasses, etc. bound up with the phase diagrams. The properties of slags should be examined, also in relation to their phase diagrams.

There is no treatment of such important compounds as gypsum and its hydrates.

In the chapter "Alkaline earth carbonates, oxides and hydroxides" there is no reference to the functional dependence of the decomposition pressure of CO_2 over carbonates on the absolute temperature.

There is no description of the construction of the basic types of dilatometers, and some of the methods of investigation of silicates are described in a very sketchy fashion.

In spite of this, however, it can be said that the author has achieved the difficult and responsible task which he set himself, of creating a text book of the chemistry of silica, the physical chemistry of silicates and the other compounds of importance for the technology of silicates. The book meets the contemporary requirement of ensuring a high level of technical knowledge in our silicate specialists.

I conceive that Prof. Kukolev's book will play a positive part in the training of engineer-technicians of high qualifications and will be useful to our specialists — whether engaged in production or research.

P. P. Budnikov

BOOK REVIEW

M. A. Matveev and K. M. Tkachenko. The Water-Resistance of Structural Materials Made from Gypsum and Its Improvement; Building Industry Press, Moscow, 1951, 92 pgs., price 4.10 rubles.

The wide introduction of gypsum structural items and materials has been achieved only by raising its water-resistance, hence a study of the methods by which this is done is of primary importance for the building materials industry of the USSR and, consequently, a work devoted to the aspects of the question which are of theoretical, topical, and practical interest is also important.

This book fills very definitely the existing gap in the specialized literature relative to the study of the water-resistance of gypsum materials.

The book presents a literature review based on the material published during the last ten years. This review reflects the current status of work on this question.

As a result of his own experimental investigations, the author presents a method which he has worked out for the testing of the water-resistance of gypsum articles, by means of which a numerical index can be assigned to samples; the testing is carried out under extremely rigorous conditions and in a relatively short time. The author has established that additions of lime to gypsum, or the combination of gypsum with hydraulic additions, raises the water-resistance of gypsum articles quite considerably.

The expediency of using a solution of a carbamide resin of definite concentration as a sealing liquid has been demonstrated experimentally. This method of preparing a gypsum mass ensures its normal solidification and the preparation of parts having a high mechanical strength and water-resistance.

A formula is proposed for a water-protective surface covering, which has very high adhesion and water-resistance. For making highly water-resistant parts the author recommends the use of a combination method of water protection. A classification of gypsum constructional materials is given, based on their water-resistance and the service conditions.

The importance of the work is determined mainly by the recommendation of a number of methods which permit gypsum parts to be manufactured with high water-resistance. Thus, the methods of impregnation and sealing with urea resins can be used for the casting of architectural details or the preparation of pressed facing boards. Lime-gypsum or lime-gypsum-pozzuolanic compositions may be recommended for the manufacture of cast or vibrated blocks and also for other gypsum items, intended for the exterior parts of buildings. These items may additionally be painted on one side with zinc silicate plaster, or may be sprayed with a solution of a urea resin in order to create an additional exterior water-protective layer, if this is necessary.

This book on the water-resistance of gypsum constructional materials is not without its defects and ommisions, both general and particular, of which the main ones are the following:

a) Only some of the properties of gypsum are described, and the question of the contemporary methods of production of gypsum binders is not dealt with at all;

this matter should have been dealt with by the author, if only briefly;

b) The graphs presented in the book are on a miniature scale, which cannot be considered satisfactory, since they are difficult to use;

c) The investigation of the nature of the products of solidification of gypsum in the presence of additions should have been done not only petro-graphically, but also by X-rays in order to compare the two results and make them more precise;

d) The production of resin-sealed gypsum powder is dealt with only very briefly in the book; since the production of stabilized aqueous solutions of urea resins is quite new, this should have been allotted more space;

e) There are various misprints in the book, which are not listed in the errata sheet.

This book is the first attempt in the USSR to generalize the material available in our domestic literature on the water resistance of gypsum parts. Its publication is undoubtedly timely, and fills a gap in the literature on the subject. It can be recommended to the engineering-technical workers of the building materials industry.

P. P. Budnikov

WORKS ON CHEMISTRY IN THE PUBLICATIONS OF THE INSTITUTES AND UNIVERSITIES

In the Soviet Union there are produced a considerable number of journals by research, teaching and other institutes and organizations and they frequently contain interesting papers on applied chemistry and chemical technology. In the absence of an abstract journal, it is extremely difficult to trace papers published in these journals. In this note I have made an attempt to acquaint the reader with some papers printed in 1950-1951 in the Soviet republics. I have not attempted any critical review of these publications: any critical attitude of mine to them has been exercised merely in the choice of the works to be listed.

1. **Publications of the Institute of Chemistry of the Latvian SSR, Vol.1, 1950, Riga (in Latvian and Russian).**

In this collection there are 14 papers, of which two: Yu. Eidux, A. Vaivade, A. Apinis, and B. Hofmann, "Investigation of the use of Gypsum Wastes for the Manufacture of Binding Materials", and K. Karlson, Yu. Eidux, A. Vaivade "Production of High Quality Portland Cement and Pozzuolanic Portland Cement from Local Raw Materials" are the result of a fundamental and detailed study of raw materials and of attempts to make use of them.

Four papers by N. Brakshs and his coworkers relate to an investigation of sapropel and sapropel tar.

There are three papers on analytical chemistry. The paper by A. Ievinina and E. Kautsis, "Determination of Small Quantities of Magnesium in Common Salt", is concerned with the determination of quantities of magnesium of the order of 0.06-0.00004%. The paper by G. Vanag and M. Litmann "Quantitative Determination of 2-Nitroindonediene-1,3 and its Salts" is devoted to the substance having

the formula C_6H_4<$\overset{CO}{\underset{CO}{}}$>$CHNO_2$. It gives numerous complex compounds and is used in analytical chemistry. The following paper by the same author is devoted to its compound with iodine.

The papers by G. Vanag and E. Vanag, "Alkylation of 2-Aminofluorene" and that by F. Vanag and V. Vitekh, "Molecular Compounds of Mercury Iodide with the Ethyl Ester of Iodoacetic Acid" are concerned with synthetic organic chemistry.

The extensive work of A. Shmids, carried out under the guidance of Prof. L. K. Lepin, "Oxidation of Colloidal Metals by Atmospheric Oxygen" gives a new, rapid method of investigating the corrosion of metals in solutions of different substances. The oxidation of cadmium, antimony, lead and copper sols in the presence of different electrolytes was studied: KCl, KBr, KI, KNO_3, K_2SO_4, Na_3PO_4, $NaOH$, NH_4OH, HCl, H_2SO_4, CH_3COOH, etc.

In the field of inorganic chemistry there is the paper by A. Keshan and E. Kunaks, "Barium Hydroborate", in which the preparation and some properties of this compound are described.

The long paper by Ya. Maizite, A. Klyav, and L. Kaug "Composition and Vermifugal Action of Tansy" relates to pharmaceutical chemistry.

2. **Proceedings of the Central Asian Polytechnic Institute, Tashkent, No. 2, 1950.**